

L Number	Hits	Search Text	DB	Time stamp
1	1626	((carbon or graphite) with (swnt or nano-tube or nanotube or nano-tubing or nanotubing or nano\$1tubule or (nano adj1 (tube or tubing or tubule))))	EPO; JPO; DERWENT	2003/10/01 09:43
2	321616	(suspension or colloid or sol or colloidal or sol-gel)	EPO; JPO; DERWENT	2003/10/01 09:43
3	40	((((carbon or graphite) with (swnt or nano-tube or nanotube or nano-tubing or nanotubing or nano\$1tubule or (nano adj1 (tube or tubing or tubule)))))) and ((suspension or colloid or sol or colloidal or sol-gel) )	EPO; JPO; DERWENT	2003/10/01 09:34
4	5	(align or aligned or aligning or parallelize or parallel or parallelizing or array or perpendicular) and (((carbon or graphite) with (swnt or nano-tube or nanotube or nano-tubing or nanotubing or nano\$1tubule or (nano adj1 (tube or tubing or tubule)))))) and ((suspension or colloid or sol or colloidal or sol-gel) )	EPO; JPO; DERWENT	2003/10/01 09:44
5	422	((carbon or graphite) with (swnt or nano-tube or nanotube or nano-tubing or nanotubing or nano\$1tubule or (nano adj1 (tube or tubing or tubule))))).ti,ab.	USPAT; US-PGPUB	2003/10/01 09:53
6	139544	(chemical or chemically) near2 (treatment or treat or treated or treating) or functionalize or functionalizing or functionalized or functional-group or (functional adj1 group)	USPAT; US-PGPUB	2003/10/01 09:43
7	1707	((carbon or graphite) with (swnt or nano-tube or nanotube or nano-tubing or nanotubing or nano\$1tubule or (nano adj1 (tube or tubing or tubule))))	USPAT; US-PGPUB	2003/10/01 09:43
8	64	((chemical or chemically) near2 (treatment or treat or treated or treating) or functionalize or functionalizing or functionalized or functional-group or (functional adj1 group)) with (((carbon or graphite) with (swnt or nano-tube or nanotube or nano-tubing or nanotubing or nano\$1tubule or (nano adj1 (tube or tubing or tubule))))))	USPAT; US-PGPUB	2003/10/01 09:43
9	418798	(suspension or colloid or sol or colloidal or sol-gel)	USPAT; US-PGPUB	2003/10/01 09:44
10	35	((((chemical or chemically) near2 (treatment or treat or treated or treating) or functionalize or functionalizing or functionalized or functional-group or (functional adj1 group)) with (((carbon or graphite) with (swnt or nano-tube or nanotube or nano-tubing or nanotubing or nano\$1tubule or (nano adj1 (tube or tubing or tubule)))))) and ((suspension or colloid or sol or colloidal or sol-gel) )	USPAT; US-PGPUB	2003/10/01 09:44
11	23	(align or aligned or aligning or parallelize or parallel or parallelizing or array or perpendicular) and (((chemical or chemically) near2 (treatment or treat or treated or treating) or functionalize or functionalizing or functionalized or functional-group or (functional adj1 group)) with (((carbon or graphite) with (swnt or nano-tube or nanotube or nano-tubing or nanotubing or nano\$1tubule or (nano adj1 (tube or tubing or tubule)))))) and ((suspension or colloid or sol or colloidal or sol-gel) )	USPAT; US-PGPUB	2003/10/01 09:45
12	11	((((carbon or graphite) with (swnt or nano-tube or nanotube or nano-tubing or nanotubing or nano\$1tubule or (nano adj1 (tube or tubing or tubule))))).ti,ab.) and ((align or aligned or aligning or parallelize or parallel or parallelizing or array or perpendicular) and (((chemical or chemically) near2 (treatment or treat or treated or treating) or functionalize or functionalizing or functionalized or functional-group or (functional adj1 group)) with (((carbon or graphite) with (swnt or nano-tube or nanotube or nano-tubing or nanotubing or nano\$1tubule or (nano adj1 (tube or tubing or tubule)))))) and ((suspension or colloid or sol or colloidal or sol-gel) )	USPAT; US-PGPUB	2003/10/01 09:45
13	0	((carbon or graphite) with (swnt or nano-tube or nanotube or nano-tubing or nanotubing or nano\$1tubule or (nano adj1 (tube or tubing or tubule))))).ti,ab.) and kuper.in.	USPAT; US-PGPUB	2003/10/01 09:54

US-PAT-NO: 6074561

DOCUMENT-IDENTIFIER: US 6074561 A

TITLE: Apparatus and method for recovering photoresist  
developers and strippers

----- KWIC -----

Detailed Description Text - DETX (24):

This invention employs several technologies together. Rigid porous membranes made from ceramics, carbon, or stainless steel support various rare earth-impregnated oxides using sol-gel process to achieve a very low fouling, back flushable, and high temperature, stable ultrafiltration or microfiltration modules.

US-PAT-NO: 6019803

DOCUMENT-IDENTIFIER: US 6019803 A

TITLE: Method for making carbon/ceramic composite electrodes  
for charge storage units

----- KWIC -----

Abstract Text - ABTX (1):

An electrochemical supercapacitor or lithium ion intercalation battery formed from carbon particles distributed in a carbon/ceramic composite paste preferably produced by sol-gel technology wherein the paste is shaped and contacted with a solvent and electrolyte salt followed by an optional washing with an aqueous or non-aqueous solution to remove residual organic solvent and salt and leaving a shaped composite having the internal microscopic surface area electrochemically accessible and useful for charge storage applications.

Brief Summary Text - BSTX (3):

The present invention relates to charge storage devices, such as electrochemical supercapacitors and lithium ion intercalation batteries, and to methods of preparation thereof. In particular, the invention relates to carbon/ceramic composites produced by sol-gel technology wherein the composite is pretreated with a solvent and an electrolyte salt which enables electrochemical accessibility to the internal microscopic surface area of the composite and form an electrode for charge storage units.

Brief Summary Text - BSTX (12):

In one embodiment of the invention, carbon/ceramic composites such as obtained by sol-gel technology are formed into a desired shape, for example a film, and contacted with a solution comprising an organic solvent and an electrolyte salt followed by washing with an aqueous solution to remove residual solvent and electrolyte salt and form a composite having a high active surface area that is electrochemically accessible and useful for supercapacitors in aqueous electrolyte solutions. In this embodiment, the preferred contacting solution is propylene carbonate as solvent and the preferred salt is tetrabutylammonium tetrafluoroborate (TBA(BF.sub.4)). The

preferred aqueous solution in this embodiment for supercapacitors is 1 M LiClO<sub>4</sub>.

Brief Summary Text - BSTX (13):

In a further embodiment of the invention, **carbon/ceramic** composites such as obtained by **sol-gel** technology are formed into a desired shape, e.g., a film on a substrate, and contacted, e.g., immersed, with an organic solvent and an electrolyte salt to form a **carbon/ceramic** composite film having a high surface area useful for supercapacitors and lithium ion intercalation electrodes in non-aqueous battery applications. In this embodiment propylene carbonate is the preferred solvent and TBA(BF<sub>4</sub>) and LiClO<sub>4</sub> are preferred electrolyte salts for the supercapacitors and lithium ion batteries respectively.

Brief Summary Text - BSTX (17):

**Carbon/ceramic** composites for treatment according to the invention are preferably fabricated using a **sol-gel** method to prepare the **ceramic network in which the carbon** particles are interspersed. The silica sol is prepared by mixing an alkoxy silane precursor with methanol as solvent and hydrochloric acid as catalyst. The sol is then mixed with a high concentration of carbon particles which, after gelation, are incorporated in the resulting ceramic network. The gelation occurs through hydroxylation of the precursor by water in ambient air, and subsequent polymerization is achieved through condensation reactions in which alkanols are formed.

Claims Text - CLTX (8):

5. A method for producing electrochemical non-aqueous supercapacitors and lithium ion electrodes for intercalation batteries from a **sol-gel** derived **carbon/ceramic** composite which comprises contacting an electrode formed into a desired shape from the composite with a liquid solution comprising an organic solvent and an electrolyte salt in an amount and for a time sufficient to wet internal microscopic surface area of the electrode, and washing the electrode with an organic solution to remove residual organic solvent and electrolyte salt and form an electrode having substantially an entire microscopic surface area electrochemically accessible and being useful for non-aqueous superconductors and lithium ion intercalation batteries.

Claims Text - CLTX (10):

7. A method for producing electrochemical non-aqueous supercapacitors and

lithium ion electrodes for intercalation batteries from a sol-gel derived carbon/ceramic composite which comprises immersing an electrode formed into a desired shape from the composite into a liquid solution comprising an organic solvent and an electrolyte salt in an amount and for a time sufficient to wet internal microscopic surface area of the electrode, and optionally, washing the electrode with an organic solution to remove residual organic solvent and electrolyte salt and form an electrode having substantially an entire microscopic surface area electrochemically accessible and being useful for non-aqueous superconductors and lithium ion intercalation batteries.

US-PAT-NO: 5753135

DOCUMENT-IDENTIFIER: US 5753135 A

TITLE: Apparatus and method for recovering photoresist  
developers and strippers

----- KWIC -----

Detailed Description Text - DETX (24):

This invention employs several technologies together. Rigid porous membranes made from ceramics, carbon, or stainless steel support various rare earth-impregnated oxides using sol-gel process to achieve a very low fouling, back flushable, and high temperature, stable ultrafiltration or microfiltration modules.

## Yao, Sam

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**From:** Aftergut, Jeff  
**Sent:** Wednesday, October 01, 2003 1:17 PM  
**To:** Maki, Steve; Yao, Sam  
**Subject:** FW: Classification / Assignment / Transfer Training

-----Original Message-----

**From:** Banks, Marilyn  
**Sent:** Wednesday, October 01, 2003 12:04 PM  
**To:** Aftergut, Jeff; Baxter, Janet; Beck, Shrive; Bell, Mark; Caldarola, Glenn; Cano, Milton; Gupta, Yogendra; Huff, Mark; Jones, Deborah (Art Unit 1775); Kelly, Cynthia; Mills, Gregory; Morris, Terrel; Nguyen, Nam; Norton, Nadine; Pyon, Harold; Silverman, Stanley; Thibodeau, Paul; Colaianni, Michael; Copenheaver, Blaine; Crispino, Richard; Dawson, Robert; Dunn, Tom; Griffin, Steven; Gulakowski, Randy; Jagannathan, Vasu; King, Roy; Ryan, Patrick; Seidleck, James; Utech, Benjamin; Walker, Wanda; Warden, Jill; Warden, Robert; Wu, David  
**Cc:** Bolling, Amy  
**Subject:** FW: Classification / Assignment / Transfer Training

Good Morning  
See instructions below:

Here is the training schedule for non IFW SPEs and examiners who will need to classify and assign the new cases that have been scanned into IFW. Please forward this to your SPEs and have them forward it to the examiners who do the classification/assignment/transfer of new cases.

If your AU is being transitioned into IFW, you will be trained in the classification, assignment and transfer procedures in your regular SIRA scheduled IFW training session.

Also, we will be adding those examiners who were trained in September in IFW Classification/Assignment/Transfer to the system and pushing the software to them beginning next week.

The following classes have been added to ATOM:

Course Title	Date	Time	Location
IFW Classification and Transfer Practices (1 HR)	10/21/2003	10:00 AM	CPK2-200
IFW Classification and Transfer Practices (1 HR)	10/21/2003	01:30 PM	CPK2-200
IFW Classification and Transfer Practices (1 HR)	10/23/2003	10:00 AM	CPK2-200
IFW Classification and Transfer Practices (1 HR)	10/23/2003	01:30 PM	CPK2-200
IFW Classification and Transfer Practices (1 HR)	10/27/2003	10:00 AM	CPK2-200
IFW Classification and Transfer Practices (1 HR)	10/27/2003	01:30 PM	CPK2-200
IFW Classification and Transfer Practices (1 HR)	10/29/2003	10:00 AM	CPK2-200
IFW Classification and Transfer Practices (1 HR)	10/29/2003	01:30 PM	CPK2-200

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Here are more detailed instructions for logging on to register for the class.

Link for access to ATOM:

<<<http://ws03932/cfdocs/siraedapp/siraatom/myaccount/signon.cfm?Source=MyAccount>>>

The name of the class is:

**IFW Classification and Transfer Practices (1 HR)**

The SPEs/examiners will follow the steps below:

Click **My Account**

Log onto your account using employee id and password.

Then click **Course Description and Schedule**

The class is sorted by Group and Title: Course Group is **Additional Course**

Then choose the class **IFW Classification and Transfer Practices (1 HR)**

Click the small (+) in the box beside the folder that contain the class sessions and choose your preferred class session.

Document ID	Title
1 US 20030102222 A1	Deposition method for nanosh
2 US 20030089893 A1	Polymers containing functiona
3 US 20030012723 A1	Spatial localization of dispers
4 US 20020150529 A1	Single-wall carbon nanotubes

DOCUMENT-IDENTIFIER: US 20030102222 A1

TITLE: Deposition method for nanostructure materials

Times New Roman 12

#### Abstract Paragraph - ABTX (1):

A method for depositing a coating of a nanostructure material onto a substrate includes: (1) forming a solution or suspension of containing the nanostructure material; (2) selectively adding "chargers" to the solution; (3) immersing electrodes in the solution, the substrate upon which the nanostructure material is to be deposited acting as one of the electrodes; (4) applying a direct and/or alternating current electrical field between the two electrodes for a certain period of time thereby causing the nanostructure materials in the solution to migrate toward and attach themselves to the substrate electrode; and (5) subsequent optional processing of the coated substrate.

#### Summary of Invention Paragraph - BSTX (23):

[0021] (i) forming a suspension of pre-formed nanostructure-containing material in a liquid medium;

#### Summary of Invention Paragraph - BSTX (25):

[0023] (iii) immersing two electrodes in the suspension, wherein at least one of the electrodes comprises the substrate; and

#### Summary of Invention Paragraph - BSTX (29):

[0027] (i) forming a suspension of pre-formed nanostructure-containing material in a liquid medium;

(19) United States  
(12) Patent Application Publication (10) Pub. No.: US 2003/0102222 A1  
Zhou et al. (43) Pub. Date: Jun. 5, 2003

(54) DEPOSITION METHOD FOR  
NANOSTRUCTURE MATERIALS

(52) U.S. CL. 203/109; 205/123; 205/67

(76) Inventors: Otto Z. Zhou, Chapel Hill, NC (US);  
Bo Gao, Carboro, NC (US); Guozhen  
Yue, Carboro, NC (US); Songlin Oh,  
Carboro, NC (US)

(57) ABSTRACT

#### Correspondence Address:

Ronald L. Grudnick  
BURNS, DOANE, SWECKER & MATHIS,  
L.L.P.  
P.O. Box 1404  
Alexandria, VA 22313-1404 (US)

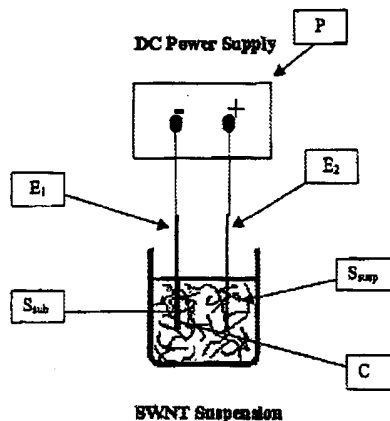
(21) App. No.: 09/996,695

(22) Filed: Nov. 30, 2001

Publication Classification

(51) Int. Cl. C25D 13/00

A method for depositing a coating of a nanostructure material onto a substrate includes: (1) forming a solution or suspension of containing the nanostructure material; (2) selectively adding "chargers" to the solution; (3) immersing electrodes in the solution, the substrate upon which the nanostructure material is to be deposited acting as one of the electrodes; (4) applying a direct and/or alternating current electrical field between the two electrodes for a certain period of time thereby causing the nanostructure materials in the solution to migrate toward and attach themselves to the substrate electrode, and (5) subsequent optional processing of the coated substrate.



Document ID	Title
5 US 20020130353 A1	Nanoscope wire-based device
6 US 20020130311 A1	Doped elongated semiconductor
7 US 20020122765 A1	Carbon nanotube structures and method for manufacturing the same
8 US 20020086124 A1	Chemical derivatization of single-walled carbon nanotubes

DOCUMENT-IDENTIFIER: US 20020122765 A1

TITLE: Carbon nanotube structures and method for manufacturing the same

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KWIC

## Summary of Invention Paragraph - BSTX (8):

[0007] Apart from this, the carbon nanotubes discovered recently are made of a tubular material with a thickness of 1 .mu.m smaller (in diameter). Ideally, a carbon face of a hexagon mesh forms a tube in parallel to an axis of the tube and multiple tubes may be formed. It may be theoretically estimated that the carbon nanotubes have either metallic or semiconductor property depending on how carbon hexagon meshes are linked and the thickness of the tubes, allowing expectation that it will be a promising functional material.

## Summary of Invention Paragraph - BSTX (11):

[0010] Finer than carbon fibers, the material with 1 .mu.m or smaller of diameter is generally called a carbon nanotube and distinguished from the carbon fiber, although no clear line can be run between both the types of carbon fibers. By a narrow definition, the material, of which carbon faces with hexagon meshes are almost parallel to the axis of the tube, is called a carbon nanotube and even a variant of the carbon nanotube, around which amorphous carbon and metal catalyst surrounds, is included in the carbon nanotube. (Note that with respect to the present invention, this narrow definition is applied to the carbon nanotube.)

## Summary of Invention Paragraph - BSTX (13):

[0012] The carbon fibers have larger diameters and incomplete cylindrical mesh structures parallel to the axes of the tubes. The carbon nanotubes produced by a vapor-phase pyrolysis method using a catalyst have a tubular mesh structure parallel to the axis of the tube in the vicinity of a center of the



US 20020122765A1

(19) United States

(12) Patent Application Publication (10) Pub. No.: US 2002/0122765 A1

Horiuchi et al.

(43) Pub. Date:

Sep. 5, 2002

(54) CARBON NANOTUBE STRUCTURES AND METHOD FOR MANUFACTURING THE SAME

(30) Foreign Application Priority Data  
Mar. 2, 2001 (JP) 2001-059053(75) Inventors: Kazunaga Horiuchi,  
Mitsumasa Horiuchi (JP); Hisao  
Yoshizawa, Mitsumasa Horiuchi (JP);  
Masashi Shimizu, Naoki Masuda (JP)Publication Classification  
(51) Int. Cl.<sup>7</sup> B32B 1/00  
(52) U.S. Cl. 423/447.1; 156/156Correspondence Address:  
CLIFF & HERRIDGE, PLC  
P.O. BOX 19428  
ALEXANDRIA, VA 22320 (US)(57) ABSTRACT  
Carbon nanotube structures which enhance handling of carbon nanotubes, enabling them to be applied in a wide variety of fields such as electronic devices, functional materials, and structural materials containing carbon nanotubes, and a method for producing them are provided. A method for manufacturing carbon nanotube structures includes the step of forming liquid bridges of a liquid at gaps among plural objects and/or at plural gaps among portions of an object. The plural carbon nanotubes are dispersed in the liquid and linked together, then arranged structurally to the liquid bridges, and the carbon nanotube structures are manufactured in this way.

(73) Assignee: FUJIFILM CO., LTD., Tokyo (JP)

(21) Appl. No. 10/814,556

(22) Filed: Dec. 14, 2001

Document ID	Title
6 US 20020130311 A1	Doped elongated semiconduct
7 US 20020122765 A1	Carbon nanotube structures an
8 US 20020086124 A1	Chemical derivatization of sin
9 US 2002004028 A1	Chemical derivatization of sin

DOCUMENT-IDENTIFIER: US 20020086124 A1

TITLE: Chemical derivatization of single-wall carbon nanotubes to facilitate solvation thereof; and use of derivatized containing seed materials for

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## Abstract Paragraph - ABTX (1):

This invention is directed to making chemical derivatives of carbon nanotubes and to uses for the derivatized nanotubes, including making arrays as a basis for synthesis of carbon fibers. In one embodiment, this invention also provides a method for preparing single wall carbon nanotubes having substituents attached to the side wall of the nanotube by reacting single wall carbon nanotubes with fluorine gas and recovering fluorine derivatized carbon nanotubes, then reacting fluorine derivatized carbon nanotubes with a nucleophile. Some of the fluorine substituents are replaced by nucleophilic substitution. If desired, the remaining fluorine can be completely or partially eliminated to produce single wall carbon nanotubes having substituents attached to the side wall of the nanotube. The substituents will, of course, be dependent on the nucleophile, and preferred nucleophiles include alkyl lithium species such as methyl lithium. Alternatively, fluorine may be fully or partially removed from fluorine derivatized carbon nanotubes by reacting the fluorine derivatized carbon nanotubes with various amounts of hydrazine, substituted hydrazine or alkyl amine. The present invention also provides seed materials for growth of single wall carbon nanotubes comprising a plurality of single wall carbon nanotubes or short tubular molecules having a catalyst precursor moiety covalently bound or physisorbed on the outer surface of the sidewall to provide the optimum metal cluster size under conditions that result in migration of the metal moiety to the tube end.

## Summary of Invention Paragraph - BSTX (3):

## (19) United States

## (12) Patent Application Publication

(10) Pub. No.: US 2002/0086124 A1

Margrave et al.

(43) Pub. Date:

Jul. 4, 2002

(54) CHEMICAL DERIVATIZATION OF SINGLE-WALL CARBON NANOTUBES TO FACILITATE SOLVATION THEREOF; AND USE OF DERIVATIZED NANOTUBES TO FORM CATALYST-CONTAINING SEED MATERIALS FOR USE IN MAKING CARBON FIBERS

(57) U.S. CL.

42836.9

## (57) ABSTRACT

This invention is directed to making chemical derivatives of carbon nanotubes and to uses for the derivatized nanotubes, including making arrays as a basis for synthesis of carbon fibers. In one embodiment, this invention also provides a method for preparing single wall carbon nanotubes having substituents attached to the side wall of the nanotube by reacting single wall carbon nanotubes with fluorine gas and recovering fluorine derivatized carbon nanotubes, then reacting fluorine derivatized carbon nanotubes with a nucleophile. Some of the fluorine substituents are replaced by nucleophilic substitution. If desired, the remaining fluorine can be completely or partially eliminated to produce single wall carbon nanotubes having substituents attached to the side wall of the nanotube. The substituents will, of course, be dependent on the nucleophile, and preferred nucleophiles include alkyl lithium species such as methyl lithium. Alternatively, fluorine may be fully or partially removed from fluorine derivatized carbon nanotubes by reacting the fluorine derivatized carbon nanotubes with various amounts of hydrazine, substituted hydrazine or alkyl amine. The present invention also provides seed materials for growth of single wall carbon nanotubes comprising a plurality of single wall carbon nanotubes or short tubular molecules having a catalyst precursor moiety covalently bound or physisorbed on the outer surface of the sidewall to provide the optimum metal cluster size under conditions that result in migration of the metal moiety to the tube end.

(76) Inventors: John L. Margrave, Bellair, TX (US); Edward T. Mitchem, Pearland, TX (US); Robert Haugs, Houston, TX (US); Peter Bowl, Houston, TX (US); Chad Huffman, Houston, TX (US); Jia Liu, Chapel Hill, NC (US); Richard E. Smalley, Houston, TX (US); Ken Smith, Kary, TX (US); Daniel T. Colbert, Houston, TX (US)

Correspondence Address:  
Winstead Sechrist & Minick P.C.  
Attn: Ross Spencer Gursam  
Suite 800  
100 Congress Avenue  
Austin, TX 78701 (US)

(21) Appl. No.: 09/810,150

(22) Filed: Mar. 16, 2001

Publication Classification

(51) Int. Cl.<sup>7</sup> B32B 1/08

DOCUMENT-IDENTIFIER: US 20020004028 A1

TITLE: Chemical derivatization of single-wall carbon nanotubes to facilitate solvation thereof; and use of derivatized nanotubes to form catalyst-containing seed materials for use in making carbon fibers

----- KWIC -----

Abstract Paragraph - ABTX (1):

This invention is directed to making chemical derivatives of carbon nanotubes and to uses for the derivatized nanotubes, including making arrays as a basis for synthesis of carbon fibers. In one embodiment, this invention also provides a method for preparing single wall carbon nanotubes having substituents attached to the side wall of the nanotube by reacting single wall carbon nanotubes with fluorine gas and recovering fluorine derivatized carbon nanotubes, then reacting fluorine derivatized carbon nanotubes with a nucleophile. Some of the fluorine substituents are replaced by nucleophilic substitution. If desired, the remaining fluorine can be completely or partially eliminated to produce single wall carbon nanotubes having substituents attached to the side wall of the nanotube. The substituents will, of course, be dependent on the nucleophile, and preferred nucleophiles include alkyl lithium species such as methyl lithium. Alternatively, fluorine may be fully or partially removed from fluorine derivatized carbon nanotubes by reacting the fluorine derivatized carbon nanotubes with various amounts of hydrazine, substituted hydrazine or alkyl amine. The present invention also provides seed materials for growth of single wall carbon nanotubes comprising a plurality of single wall carbon nanotubes or short tubular molecules having a catalyst precursor moiety covalently bound or physisorbed on the outer surface of the sidewall to provide the optimum metal cluster size under conditions that result in migration of the metal moiety to the tube end.

Summary of Invention Paragraph - BSTX (3):

[0002] This invention is directed to making chemical derivatives of carbon nanotubes and to uses for the derivatized nanotubes, including making arrays as a basis for synthesis of carbon fibers.

Summary of Invention Paragraph - BSTX (9):

[0008] An improved method of producing single-wall nanotubes is described in U.S. Ser. No. 08/687,665, entitled "Ropes of Single-Walled Carbon Nanotubes" incorporated herein by reference in its entirety. This method uses, inter alia, laser vaporization of a graphite substrate doped with transition metal atoms, preferably nickel, cobalt, or a mixture thereof, to produce single-wall carbon nanotubes in yields of at least 50% of the condensed carbon. The single-wall nanotubes produced by this method tend to be formed in clusters, termed "ropes," of 10 to 1000 single-wall carbon nanotubes in **parallel** alignment, held together by van der Waals forces in a closely packed triangular lattice. Nanotubes produced by this method vary in structure, although one structure tends to predominate.

Summary of Invention Paragraph - BSTX (10):

[0009] A method of producing carbon fibers from single-wall carbon nanotubes is described in PCT Patent Application No. PCT/US98/04513, incorporated herein by reference in its entirety. The carbon fibers are produced using SWNT molecules in a substantially two-dimensional **array** made up of single-walled nanotubes aggregated (e.g., by van der Waals forces) in substantially **parallel** orientation to form a monolayer extending in directions substantially **perpendicular** to the orientation of the individual nanotubes. In this process the seed **array** tubes are opened at the top (free) end and a catalyst cluster is deposited at this free end. A gaseous carbon source is then provided to grow the nanotube assembly into a fiber. In various processes involving metal cluster catalysis, it is important to provide the proper number of metal atoms to give the optimum size cluster for single wall nanotube formation.

Summary of Invention Paragraph - BSTX (12):

[0011] Since the discovery of single wall carbon nanotubes (SWNTs) in 1993 (Iijima, S. and Ichihashi, T., Nature 1993,363:603-605), researchers have been searching for ways to manipulate them chemically. While there have been many reports and review articles on the production and physical properties of carbon nanotubes, reports on chemical manipulation of nanotubes have been slow to emerge. There have been reports of **functionalizing** nanotube ends with carboxylic groups (Rao, et al., Chem. Commun., 1996,1525-1526; Wong, et al., Nature, 1998,394:52-55), and then further manipulation to tether them to gold particles via thiol linkages (Liu, et al., Science, 1998, 280:1253-1256). Haddon and co-workers (Chen, et al., Science, 1998, 282:95-98) have reported solvating SWNTs by adding octadecylamine groups on the ends of the tubes and then adding dichlorocarbenes to the nanotube side wall, albeit in relatively low quantities (.about.2%). While theoretical results have suggested that

functionalization of the nanotube side-wall is possible (Cahill, et al., Tetrahedron, 1996, 52 (14):5247-5256), experimental evidence confirming this theory has not been obtained.

Summary of Invention Paragraph - BSTX (20):

[0018] This invention also provides a process for preparing a suspension or solution of single wall carbon nanotubes in various solvents from which individual single wall carbon nanotubes may be isolated, the process comprising providing a mass of single wall carbon nanotubes that include bundles of fibers held in close association by van der Waals forces, derivatizing the side walls of the single wall carbon nanotubes with a plurality of chemical moieties distributed substantially uniformly along the length of said single wall carbon nanotube side walls, said chemical moieties having chemical and steric properties sufficient to prevent the reassembly of van der Waals force bound bundles, producing true solutions and recovering the individual, derivatized single wall carbon nanotubes from said solution or suspension. Preferably, the attached chemical moieties are fluorine to provide solution in various alcohols, preferably isopropyl alcohol, and various R-groups to appropriate to provide solubility in other solvents including CHCl<sub>3</sub>, Dimethylformamide, etc.

Summary of Invention Paragraph - BSTX (21):

[0019] In another embodiment, a method for forming a macroscopic molecular array of tubular carbon molecules is disclosed. This method includes the steps of providing at least about 10<sup>6</sup> tubular carbon molecules of substantially similar length in the range of 50 to 500 nm; introducing a linking moiety onto at least one end of the tubular carbon molecules; providing a substrate coated with a material to which the linking moiety will attach; and contacting the tubular carbon molecules containing a linking moiety with the substrate.

Summary of Invention Paragraph - BSTX (23):

[0021] This invention also provides a seed array for the catalytic production of assemblies of single wall carbon nanotubes comprising a plurality of relatively short single wall carbon nanotubes assembled in a generally parallel configuration, and disposed on the side wall of each said single wall carbon nanotube a sufficient quantity of physisorbed or covalently bonded transition metal catalyst precursor moieties to provide active catalyst metal atom clusters of the proper size to grow single wall carbon nanotubes under conditions that promote the generation of metal atoms and the migration of said metal atoms to the free ends of said single wall carbon nanotubes.

Summary of Invention Paragraph - BSTX (24):

[0022] In another embodiment, a method for continuously growing a macroscopic carbon fiber comprising at least about 10.sup.6 single-wall nanotubes in generally parallel orientation is disclosed. In this method, a macroscopic molecular array of at least about 10.sup.6 tubular carbon molecules in generally parallel orientation is provided. The array is processed to provide a single plane of open-ended nanotubes at an angle generally perpendicular to the axes of parallel tubes in the array. The open ends of the tubular carbon molecules in the array are then contacted with a catalytic metal by causing migration of metal atoms released from side wall attached catalyst precursor groups. A gaseous source of carbon is supplied to the end of the array while localized energy is applied to the end of the array in order to heat the end to a temperature in the range of about 500.degree. C. to about 1300.degree. C. . The growing carbon fiber is continuously recovered.

Summary of Invention Paragraph - BSTX (25):

[0023] In another embodiment, an apparatus for forming a continuous macroscopic carbon fiber from a macroscopic molecular template array similar to that described above, comprising at least about 10.sup.6 single-wall carbon nanotubes having a catalytic metal deposited on the open ends of said nanotubes is disclosed. This apparatus includes a means for locally heating only the open ends of the nanotubes in the template array in a growth and annealing zone to a temperature in the range of about 500.degree. C. to about 1300.degree. C. It also includes a means for supplying a carbon-containing feedstock gas to the growth and annealing zone immediately adjacent the heated open ends of the nanotubes in the template array. It also includes a means for continuously removing growing carbon fiber from the growth and annealing zone while maintaining the growing open end of the fiber in the growth and annealing zone.

Brief Description of Drawings Paragraph - DRTX (19):

[0042] FIG. 14 is a schematic representation of a portion of an homogeneous SWNT molecular array according to the present invention.

Brief Description of Drawings Paragraph - DRTX (20):

[0043] FIG. 15 is a schematic representation of an heterogeneous SWNT molecular array according to the present invention.

Brief Description of Drawings Paragraph - DRTX (23):

[0046] FIG. 18 is a composite array according to the present invention.

Brief Description of Drawings Paragraph - DRTX (24):

[0047] FIG. 19 is a composite array according to the present invention.

Detail Description Paragraph - DETX (6):

[0052] In defining carbon nanotubes, it is helpful to use a recognized system of nomenclature. In this application, the carbon nanotube nomenclature described by M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, Science of Fullereness and Carbon Nanotubes, Chap. 19, especially pp. 756-760, (1996), published by Academic Press, 525 B Street, Suite 1900, San Diego, Calif. 92101-4495 or 6277 Sea Harbor Drive, Orlando, Fla. 32877 (ISBN 0-12-221820-5), which is hereby incorporated by reference, will be used. The single wall tubular fullerenes are distinguished from each other by double index (n,m) where n and m are integers that describe how to cut a single strip of hexagonal "chicken-wire" graphite so that it makes the tube perfectly when it is wrapped onto the surface of a cylinder and the edges are sealed together. When the two indices are the same,  $m=n$ , the resultant tube is said to be of the "arm-chair" (or n,n) type, since when the tube is cut perpendicular to the tube axis, only the sides of the hexagons are exposed and their pattern around the periphery of the tube edge resembles the arm and seat of an arm chair repeated n times. Arm-chair tubes are a preferred form of single-wall carbon nanotubes since they are metallic, and have extremely high electrical and thermal conductivity. In addition, all single-wall nanotubes have extremely high tensile strength.

Detail Description Paragraph - DETX (54):

[0100] The present inventors have, for the first time, functionalized the sidewalls of SWNTs by reacting them with elemental fluorine. The inventors have discovered that fluorine could be added to the side wall of carbon nanotubes yielding stoichiometries up to approximately C.sub.2F without destruction of the tube-like structure. The inventors have also discovered that a high degree of solvation can be achieved by sonicating fluorinated SWNTs in a variety of alcohol solvents such as methanol, ethanol, and isopropanol. As demonstrated herein, reactions can be carried out on these nanotubes while in solution by reacting them with hydrazine which serves as a defluorinating agent. It has also been demonstrated that these "fluorotubes" can be reacted with sodium methoxide (a strong nucleophile) while in solution to form methoxylated SWNTs.

Detail Description Paragraph - DETX (56):

[0102] The inventors have further demonstrated that once solvated, these fluorotubes can then be reacted with species while in solution to either defluorinate or further **functionalize** them. The chemistry possible with these solvated fluorotubes provides an important route to the synthesis of a wide variety of **functionalized** nanotubes having many different and useful properties.

Detail Description Paragraph - DETX (60):

[0104] 1.1 Fluorination of Single-wall Carbon Nanotubes Single-walled carbon nanotubes were produced by the dual pulsed laser vaporization of Co/Ni doped graphite rods and purified by techniques described previously (Rinzler, et al., 1998). The purification product is a metastable **colloidal suspension** of SWNT "ropes" (bundles of hexagonally close packed tubes ranging from a few to 200 SWNT, See Thess, et al., 1996) in a 0.2% aqueous solution of Triton X-100 surfactant. Filtering the solution through a PTFE filter membrane and washing with methanol to remove residual surfactant leaves a black film on the surface. If this layer is sufficiently thick (10-75  $\mu\text{m}$ ) it can be peeled off to form a free standing film or "bucky paper" of SWNT. This form has appreciable mechanical integrity and is convenient for handling, and for electrical conductivity and Raman scattering measurements. It is the fluorination of this "bucky paper" that is described here.

Detail Description Paragraph - DETX (78):

[0121] The electrical properties of the SWNT change dramatically as they are **functionalized**. The untreated SWNT are essentially metallic and their two point resistance (essentially a contact resistance, Bozhko, et al., 1998, Appl. Phys. A, 67:75-77) measured across 5 mm of the "bucky paper" surface is 10-15  $\Omega$ . When fluorinated, the tubes become insulating and the two point resistance exceeds 20 M  $\Omega$ . After methylation the tubes possess a two point resistance of about 20 k $\Omega$ . Pyrolysis of the methylated product brings the resistance down to about 100  $\Omega$ . Incomplete return of the electrical conductivity upon pyrolysis may be due to an increased contact resistance that results from disorder induced into the rope lattice following the sequence of reaction steps.

Detail Description Paragraph - DETX (79):

[0122] The methylated SWNT could be suspended quite readily by sonication in

chloroform. Dispersal of this suspension on a Si wafer followed by AFM analysis confirmed the nondestructive nature of the sonication process. Additionally, a large number of single tubes could be seen. This -was not true of similarly exposed, untreated SWNT.

Detail Description Paragraph - DETX (85):

[0127] Single wall carbon nanotubes were produced by the dual pulsed laser vaporization of Co/Ni doped graphite rods and purified by methods discussed previously (Rinzler, et al., Appl. Phys.A, 1998, 67:9-37.). The SWNTs produced in this way are primarily (10,10) nanotubes. The purified product is a metastable colloidal suspension of SWNT "ropes" (bundles of tubes ranging from a few to 200 SWNTs, see Thess, et al., Science 1996, 273, 483-487) in a 0.2% aqueous solution of Triton.TM. X-100 surfactant. This was then filtered over a PTTE filter membrane (Sartorius, with 0.2 .mu.m pore dimensions) and rinsed with methanol. Filtering this and rinsing with methanol leads to a final product which is a freestanding "mat" or "bucky paper" of SWNTs that is approximately 10 .mu.m thick. Purity of the SWNTs was monitored via scanning electron microscopy (JEOL 6320F SEM). FIG. 9 shows a sample of typical purity. This product was then resuspended by sonication in dimethyl formamide (DMF; Fisher, HPLC grade). Such treatment is believed to "cut" the tubes at their defect sites and also seems to unravel the ropes somewhat, leading to bundles containing fewer SWNTs. This product was then filtered, rinsed and heated in an oven at 150.degree. C. for 2 hours prior to fluorination. Sonication in DMF may result in smaller SWNT ropes and ultimately lead to a more efficient fluorination.

Detail Description Paragraph - DETX (103):

[0145] Molecular Arrays of Single-wall Carbon Nanotubes

Detail Description Paragraph - DETX (104):

[0146] An application of particular interest for a homogeneous population of SWNT molecules is production of a substantially two-dimensional array made up of single-walled nanotubes aggregating (e.g., by van der Waals forces) in substantially parallel orientation to form a monolayer extending in directions substantially perpendicular to the orientation of the individual nanotubes. Formation of such arrays is substantially enabled by derivatization of both the ends and side walls of nanotubes as is indicated below. Such monolayer arrays can be formed by conventional techniques employing "self-assembled monolayers" (SAM) or Langmuir-Blodgett films, see Hirsch, pp. 75-76. Such a molecular array is illustrated schematically in FIG. 14. In this figure, derivatized

nanotubes 1 are bound via interaction of the linking or complexing moiety attached to the nanotube to a substrate 2 having a reactive coating 3 (e.g., gold). Sidewall derivatization in this application can facilitate assembly of the array by enabling the tubes to move effectively together as the array assembles.

Detail Description Paragraph - DETX (105):

[0147] Typically, SAMs are created on a substrate which can be a metal (such as gold, mercury or ITO (indium-tin-oxide)). The molecules of interest, here the SWNT molecules, are linked (usually covalently) to the substrate through a linker moiety such as --S--, --S--(CH<sub>2</sub>)<sub>n</sub>--N--H--, --SiO<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>NH-- or the like. The linker moiety may be bound first to the substrate layer or first to the SWNT molecule (at an open or closed end) to provide for reactive self-assembly. Langmuir-Blodgett films are formed at the interface between two phases, e.g., a hydrocarbon (e.g., benzene or toluene) and water. Orientation in the film is achieved by employing molecules or linkers that have hydrophilic and lipophilic moieties at opposite ends. The configuration of the SWNT molecular array may be homogenous or heterogeneous depending on the use to which it will be put. Using, SWNT molecules of the same type and structure provides a homogeneous array of the type shown in FIG. 14. By using different SWNT molecules, either a random or ordered heterogeneous structure can be produced. An example of an ordered heterogeneous array is shown in FIG. 15 where tubes 4 are (n,n), i.e., metallic in structure and tubes 5 are (m,n), i.e., insulating. This configuration can be achieved by employing successive reactions after removal of previously masked areas of the reactive substrate.

Detail Description Paragraph - DETX (106):

[0148] Arrays containing from 10<sup>3</sup> up to 10<sup>10</sup> and more SWNT molecules in substantially parallel relationships can be used per se as a nanoporous conductive molecular membrane, e.g., for use in fuel cells and in batteries such as the lithium ion battery. This membrane can also be used (with or without attachment of a photoactive molecule such as cis-(bisthiacyanato bis (4,4'-dicarboxy-2,2'-bipyridine Ru (II))) to produce a highly efficient photo cell of the type shown in U.S. Pat. 5,084,365.

Detail Description Paragraph - DETX (107):

[0149] One preferred use of the SWNT molecular arrays of the present invention is to provide a "seed" or template for growth of macroscopic carbon fiber of single-wall carbon nanotubes as described below. The use of a

macroscopic cross section in this template is particularly useful for keeping the live (open) end of the nanotubes exposed to feedstock during growth of the fiber. The template array of this invention can be used as formed on the original substrate, cleaved from its original substrate and used with no substrate (the van der Waals forces will hold it together) or transferred to a second substrate more suitable for the conditions of fiber growth.

Detail Description Paragraph - DETX (108):

[0150] Where the SWNT molecular array is to be used as a seed or template for growing macroscopic carbon fiber as described below, the array need not be formed as a substantially two-dimensional array. The "seed" array can, for instance, be the end of a fiber of parallel nanotubes in van der Waals contact that has been cut, or a short segment of such a fiber that has been cut from the fiber. For such substrates the surface comprising the ends of must be prepared to be clean and flat by polishing and or electrochemical etching to achieve a clean, highly planar surface of exposed nanotube ends. Any form of array that presents at its upper surface a two-dimensional array can be employed. In the preferred embodiment, the template molecular array is a manipulatable length of macroscopic carbon fiber as produced below.

Detail Description Paragraph - DETX (109):

[0151] Large arrays (i.e.,  $>10^{10}$  tubes) also can be assembled using nanopipes by combining smaller arrays or by folding linear collections of tubes and/or ropes over (i.e., one folding of a collection of  $n$  tubes results in a bundle with  $2n$  tubes).

Detail Description Paragraph - DETX (111):

[0153] The present invention provides methods for growing continuous carbon fiber from SWNT molecular arrays to any desired length. The carbon fiber which comprises an aggregation of substantially parallel carbon nanotubes may be produced according to this invention by growth (elongation) of a suitable seed molecular array. As used herein, the term "macroscopic carbon fiber" refers to fibers having a diameter large enough to be physically manipulated, typically greater than about 1 micron and preferably greater than about 10 microns.

Detail Description Paragraph - DETX (116):

[0158] 3) It can enable growth of ordered structures of SWNT that have been assembled by other means (e.g., suitable arrays can be formed by conventional techniques employing "self-assembled monolayers" (SAM) or Langmuir-Blodgett

films, see Hirsch, pp. 75-76.

Detail Description Paragraph - DETX (117):

[0159] 4) It can be used to grow structural shapes of SWNT material comprising parallel nanotubes all in van der Waals contact. These materials can have the forms of sheets, I-beams, channels, etc. by appropriately configuring the seed in the shape of the cross section of the desired structural object.

Detail Description Paragraph - DETX (122):

[0164] 4) Growth of organized structures of SWNT (e.g., arrays of tubes with specific relative spacing and orientation of individual tubes, membranes of tubes comprising many parallel tubes closely packed together, and rods or fibers of tubes with parallel axes) in which an initial structure has been assembled by other means, which include the operation of molecule agencies attached to the sidewalls of the SWNTs forming the structure, and the novel compositions of matter so produced.

Detail Description Paragraph - DETX (130):

[0172] d) Formation of arrays of SWNT wherein the array formation is enabled and controlled by species attached to the tube sidewalls. This species that enables array formation may be attached to the tube by covalent bonding, chemisorption, adsorption, or a combination thereof. This aspect of this invention:

Detail Description Paragraph - DETX (133):

[0175] The first step in the growth process is to open the growth end of the SWNTs in the molecular array. This can be accomplished as described above with an oxidative and/or electrochemical treatment. Next, a transition metal catalyst is added to the open-ended seed array. The transition metal catalyst can be any transition metal that will cause conversion of the carbon-containing feedstock described below into highly mobile carbon radicals that can rearrange at the growing edge to the favored hexagon structure. Suitable materials include transition metals, and particularly the Group VI B or VIII B transition metals, i.e., chromium (Cr), molybdenum (Mo), tungsten (W), iron (Fe), cobalt (Co), nickel (Ni), ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir) and platinum (Pt). Metals from the lanthanide and actinide series may also be used. Preferred are Fe, Ni, Co and mixtures thereof. Most preferred is a 50/50 mixture (by weight) of Ni and Co.

Detail Description Paragraph - DETX (135):

[0177] In the preferred process, the catalyst is formed, in situ, on the open tube ends of the molecular array by a vacuum deposition process. Any suitable equipment, such as that used in Molecular Beam Epitaxy (MBE) deposition, can be employed. One such device is a Kudsens Effusion Source Evaporator. It is also possible to effect sufficient deposition of metal by simply heating a wire in the vicinity of the tube ends (e.g., a Ni/CO wire or separate Ni and CO wires) to a temperature below the melting point at which enough atoms evaporate from one wire surface (e.g., from about 900 to about 1300.degree. C.). The deposition is preferably carried out in a vacuum with prior outgassing. Vacuums of about 10.sup.-6 to 10.sup.-8 Torr are suitable. The evaporation temperature should be high enough to evaporate the metal catalyst. Typically, temperatures in the range of 1500 to 2000.degree. C. are suitable for the Ni/Co catalyst of the preferred embodiment. In the evaporation process, the metal is typically deposited as monolayers of metal atoms. From about 1-10 monolayers will generally give the required amount of catalyst. The deposition of transition metal clusters on the open tube tops can also be accomplished by laser vaporization of metal targets in a catalyst deposition zone.

Detail Description Paragraph - DETX (139):

[0181] In the next step of the process of the present invention, the SWNT molecular array with catalyst deposited on the open tube ends is subjected to tube growth (extension) conditions. This may be in the same apparatus in which the catalyst is deposited or a different apparatus. The apparatus for carrying out this process will require, at a minimum, a source of carbon-containing feedstock and a means for maintaining the growing end of the continuous fiber at a growth and annealing temperature where carbon from the vapor can be added to the growing ends of the individual nanotubes under the direction of the transition metal catalyst. Typically, the apparatus will also have means for continuously collecting the carbon fiber. The process will be described for illustration purposes with reference to the apparatus shown in FIGS. 16 and 17.

Detail Description Paragraph - DETX (140):

[0182] The carbon supply necessary to grow the SWNT molecular array into a continuous fiber is supplied to the reactor 10, in gaseous form through inlet 11. The gas stream should be directed towards the front surface of the growing array 12. The gaseous carbon-containing feedstock can be any hydrocarbon or mixture of hydrocarbons including alkyls, acyls, aryls, aralkyls and the like,

as defined above. Preferred are hydrocarbons having from about 1 to 7 carbon atoms. Particularly preferred are methane, ethane, ethylene, acetylene, acetone, propane, propylene and the like. Most preferred is ethylene. Carbon monoxide may also be used and in some reactions is preferred. Use of CO feedstock with transition metal catalysts is believed to follow a different reaction mechanism than that proposed for most other feedstock gasses. See Dai, et al., 1996.

Detail Description Paragraph - DETX (141):

[0183] The feedstock concentration is preferably as chosen to maximize the rate of reaction, with higher concentrations of hydrocarbon giving faster growth rates. In general, the partial pressure of the feedstock material (e.g., ethylene) can be in the 0.001 to 1000.0 Torr range, with values in the range of about 1.0 to 10 Torr being preferred. The growth rate is also a function of the temperature of the growing array tip as described below, and as a result growth temperatures and feed stock concentration can be balanced to provide the desired growth rates. A preferred feedstock in many instances is CO, in which case the optimal pressures are in the range of 10 to 100 atmospheres.

Detail Description Paragraph - DETX (143):

[0185] The SWNT molecular array tip should be heated to a temperature sufficient to cause growth and efficient annealing of defects in the growing fiber, thus forming a growth and annealing zone at the tip. In general, the upper limit of this temperature is governed by the need to avoid pyrolysis of the feedstock and fouling of the reactor or evaporation of the deposited metal catalyst. For most feedstocks and catalysts, this is below about 1300.degree. C. The lower end of the acceptable temperature range is typically about 500.degree. C., depending on the feedstock and catalyst efficiency. Preferred are temperatures in the range of about 500.degree. C. to about 1200.degree. C. More preferred are temperatures in the range of from about 700.degree. C. to about 1200.degree. C. Temperatures in the range of about 900.degree. C. to about 1100.degree. C. are the most preferred, since at these temperatures the best annealing of defects occurs. The temperature at the growing end of the cable is preferably monitored by, and controlled in response to, an optical pyrometer 14, which measures the incandescence produced. While not preferred due to potential fouling problems, it is possible under some circumstances to employ an inert sweep gas such as argon or helium.

Detail Description Paragraph - DETX (147):

[0189] The molecular array (template) may be removed from the fiber before or after growth by macroscopic physical separation means, for example by cutting the fiber with scissors to the desired length. Any section from the fiber may be used as the template to initiate production of similar fibers.

Detail Description Paragraph - DETX (148):

[0190] The continuous carbon fiber of the present invention can also be grown from more than one separately prepared molecular array or template. The multiple arrays can be the same or different with respect to the SWNT type or geometric arrangement in the array. Large cable-like structures with enhanced tensile properties can be grown from a number of smaller separate arrays as shown in FIG. 18. In addition to the masking and coating techniques described above, it is possible to prepare a composite structure, for example, by surrounding a central core array of metallic SWNTs with a series of smaller circular non-metallic SWNT arrays arranged in a ring around the core array as shown in FIG. 19.

Detail Description Paragraph - DETX (149):

[0191] Not all the structures contemplated by this invention need be round or even symmetrical in two-dimensional cross section. It is even possible to align multiple molecular array seed templates in a manner as to induce nonparallel growth of SWNTs in some portions of the composite fiber, thus producing a twisted, helical rope, for example. It is also possible to catalytically grow macroscopic carbon fiber in the presence of an electric field to aid in alignment of the SWNTs in the fibers, as described above in connection with the formation of template arrays.

Detail Description Paragraph - DETX (155):

[0197] The supported or unsupported SWNT seed materials can be combined with a suitable growth catalyst as described above, by opening SWNT molecule ends and depositing a metal atom cluster. Alternatively, the growth catalyst can be provided to the open end or ends of the seed molecules by evaporating a suspension of the seeds in a suitable liquid containing a soluble or suspended catalyst precursor. For example, when the liquid is water, soluble metal salts such as Fe (NO.sub.3).sub.3, Ni (NO.sub.3).sub.2 or CO (NO.sub.3).sub.2 and the like may be employed as catalyst precursors. In order to insure that the catalyst material is properly positioned on the open end(s) of the SWNT seed molecules, it may be necessary in some circumstances to derivatize the SWNT ends with a moiety that binds the catalyst nanoparticle or more preferably a ligand-stabilized catalyst nanoparticle.

Detail Description Paragraph - DETX (156):

[0198] In the first step of the random growth process the suspension of seed particles containing attached catalysts or associated with dissolved catalyst precursors is injected into an evaporation zone where the mixture contacts a sweep gas flow and is heated to a temperature in the range of 250-500.degree. C. to flash evaporate the liquid and provide an entrained reactive nanoparticle (i.e., seed/catalyst). Optionally this entrained particle stream is subjected to a reduction step to further activate the catalyst (e.g., heating from 300-500.degree. C. in H.sub.2). A carbonaceous feedstock gas, of the type employed in the continuous growth method described above, is then introduced into the sweep gas/active nanoparticle stream and the mixture is carried by the sweep gas into and through a growth zone.

Claims Text - CLTX (18):

18. An array of single-wall nanotubes for the catalytic production of assemblies of single wall carbon nanotubes comprising a plurality of single wall carbon nanotubes assembled in a generally parallel configuration, said nanotubes being of approximately equal length and each having at least one free end, wherein on the side wall of each said single wall carbon nanotube is disposed a quantity of physisorbed or covalently bonded transition metal catalyst precursor moieties sufficient to provide active catalyst metal atom clusters to grow single wall carbon nanotubes under conditions that promote the generation of metal atoms and the migration of said metal atoms to the free ends of said single wall carbon nanotubes.

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	Document ID	Title
1	JP 2001020093 A	ELECTROPHORESIS DEVI
2	WO 163028 A1	METHOD FOR OBTAINING
3	WO 200295097 A	Preparation of non-aligned car
4	US 20020046872 A	Composition of matter used in

PAT-NO: JP02001020093A

DOCUMENT-IDENTIFIER: JP 2001020093 A

DEVICE, ELECTRON RELEASING E  
PRODUCED BY UTILIZING THE S  
WELL AS THEIR PRODUCTION

PUBN-DATE: January 23, 2001

INVENTOR-INFORMATION:  
NAME COUNTRY  
AKIYAMA, KOJI N/A  
SHIRATORI, TETSUYA N/A

INT-CL (IPC): C25D013/00, C25D013/12, G01N027/447, H01J001/304, H01J

ABSTRACT:  

PROBLEM TO BE SOLVED: To easily gather particulates at an arbitrary point and to produce a release element provided with a cold cathode member with good productivity by forming a projecting part on either one surface of parallel flat plate electrodes which are formed by sandwiching a suspension containing the particulates between a pair of the parallel flat plate electrodes facing each other and move the particulates by impressing an electric field thereto.

SOLUTION: The flat plate electrode 103 provided with the projecting part 102 and a glass substrate 105 having an Al electrode 104 are arranged in parallel within an electrophoresis vessel 101. The suspension 107 nearly uniformly dispersed with carbon nanotubes 106 is injected into the vessel and voltage is impressed between the flat plate electrode 103 and the Al electrode 104 by a DC power source 108. The carbon nanotubes 106 tightly gathered to a spherical form on the Al electrode 104 facing the projecting part 102 and adhere to the glass substrate 105. When a light emission device is constituted 4 the glass

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	9/02	H 0 1 J 1/30	F

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(21)出願番号 特願平11-195308	(71)出願人 000035823 松下電器産業株式会社 大阪府門真市大字門真1006番地
(22)出願日 平成11年7月9日(1999.7.9)	(72)発明者 坂山 修二 大阪府門真市大字門真1006番地 松下電器産業株式会社内
	(72)発明者 白鳥 哲也 大阪府門真市大字門真1006番地 松下電器産業株式会社内
	(74)代理人 000097445 弁護士 岩間 文雄 (外2名)

(54)【発明の名称】 電気泳動装置およびそれを用いて製造した電子放出素子および画像表示装置、並びにそれらの製造方法

(57)【要約】  
【課題】 少ないプロセス工程で低コストの電子放出素子を容易に形成できる電気泳動装置を提供する。  
【解決手段】 一対の対向する平行平板電極間に微粒子を含む懸濁液をサンドイッチし、該電極間に電圧を印加して該微粒子を移動させる電気泳動装置に於て、該平行平板電極の少なくともどちらか一方の表面に突起を形成する。

101  
103  
102  
107  
104  
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108  
1000

PAT-NO: JP02001020093A

DOCUMENT-IDENTIFIER: JP 2001020093 A

TITLE: ELECTROPHORESIS DEVICE, ELECTRON RELEASING  
ELEMENT AND  
IMAGE DISPLAY DEVICE PRODUCED BY UTILIZING THE SAME  
AS  
WELL AS THEIR PRODUCTION

PUBN-DATE: January 23, 2001

INVENTOR-INFORMATION:

NAME	COUNTRY
AKIYAMA, KOJI	N/A
SHIRATORI, TETSUYA	N/A

INT-CL (IPC): C25D013/00, C25D013/12 , G01N027/447 , H01J001/304 , H01J009/02

ABSTRACT:

**PROBLEM TO BE SOLVED:** To easily gather particulates at an arbitrary point and to produce a release element provided with a cold cathode member with good productivity by forming a projecting part on either one surface of parallel flat plate electrodes which are formed by sandwiching a suspension containing the particulates between a pair of the parallel flat plate electrodes facing each other and move the particulates by impressing an electric field thereto.

**SOLUTION:** The flat plate electrode 103 provided with the projecting part 102 and a glass substrate 105 having an Al electrode 104 are arranged in parallel within an electrophoresis vessel 101. The suspension 107 nearly uniformly dispersed with carbon nanotubes 106 is injected into the vessel and voltage is impressed between the flat plate electrode 103 and the Al electrode 104 by a DC power source 108. The carbon nanotubes 106 tightly gathered to a spherical form on the Al electrode 104 facing the projecting part 102 and adhere to the glass substrate 105. When a light emission device is constituted 4 the glass substrate 105 as a cathode and an anode consisting of a phosphor thin film, the carbon nanotubes function as a cold cathode member and the phosphor thin films emit light to a planar form. The particulates may be gathered and fixed by the

fewer stages.

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Abstract Text - FPAR (1):

PROBLEM TO BE SOLVED: To easily gather particulates at an arbitrary point and to produce a release element provided with a cold cathode member with good productivity by forming a projecting part on either one surface of parallel flat plate electrodes which are formed by sandwiching a suspension containing the particulates between a pair of the parallel flat plate electrodes facing each other and move the particulates by impressing an electric field thereto.

Abstract Text - FPAR (2):

SOLUTION: The flat plate electrode 103 provided with the projecting part 102 and a glass substrate 105 having an Al electrode 104 are arranged in parallel within an electrophoresis vessel 101. The suspension 107 nearly uniformly dispersed with carbon nanotubes 106 is injected into the vessel and voltage is impressed between the flat plate electrode 103 and the Al electrode 104 by a DC power source 108. The carbon nanotubes 106 tightly gathered to a spherical form on the Al electrode 104 facing the projecting part 102 and adhere to the glass substrate 105. When a light emission device is constituted 4 the glass substrate 105 as a cathode and an anode consisting of a phosphor thin film, the carbon nanotubes function as a cold cathode member and the phosphor thin films emit light to a planar form. The particulates may be gathered and fixed by the fewer stages.

PUB-NO: WO000163028A1

DOCUMENT-IDENTIFIER: WO 163028 A1

TITLE: METHOD FOR OBTAINING MACROSCOPIC FIBRES AND STRIPS FROM  
COLLOIDAL PARTICLES AND IN PARTICULAR CARBON NANOTUBES

PUBN-DATE: August 30, 2001

INVENTOR-INFORMATION:

NAME	COUNTRY
POULIN, PHILIPPE	FR
VIGOLO, BRIGITTE	FR
PENICAUD, ALAIN	FR
COULON, CLAUDE	FR

INT-CL (IPC): D01F009/12, D01D005/00

EUR-CL (EPC): D01D005/00 ; D01F001/10, D01F009/12

ABSTRACT:

CHG DATE=20011002 STATUS=O>The invention concerns a method for obtaining fibres and strips from colloidal particles, characterised in that it consists in: 1) dispersing said particles in a solvent optionally using a surfactant; 2) injecting the resulting dispersion solution through at least an orifice emerging into a flow of an external solution, preferably, having a higher viscosity than said dispersion, the viscosity levels being measured in the same temperature and pressure conditions, so as to cause said particles to agglomerate into fibres or strips by destabilising the particle dispersions and optionally aligning said particles.

----- KWIC -----

Abstract Text - FPAR (1):

CHG DATE=20011002 STATUS=O>The invention concerns a method for obtaining

fibres and strips from colloidal particles, characterised in that it consists in: 1) dispersing said particles in a solvent optionally using a surfactant; 2) injecting the resulting dispersion solution through at least an orifice emerging into a flow of an external solution, preferably, having a higher viscosity than said dispersion, the viscosity levels being measured in the same temperature and pressure conditions, so as to cause said particles to agglomerate into fibres or strips by destabilising the particle dispersions and optionally aligning said particles.

Title of Patent Publication - TTL (1):

METHOD FOR OBTAINING MACROSCOPIC FIBRES AND STRIPS FROM  
COLLOIDAL PARTICLES  
AND IN PARTICULAR CARBON NANOTUBES



Document ID	Title
WO 163028 A1	METHOD FOR OBTAINING
WO 200295097 A	Preparation of non-aligned ca
US 20020046872 A	Composition of matter used in
WO 200130694 A	Aligning single-wall carbon n

DERWENT-ACC-NO: 2003-112154  
DERWENT-WEEK: 200310

Preparation of non-aligned carbon nanotubes in reaction vessel involves utilizing catalyst material in the form of catalytic particles

INVENTOR: LI, W; REN, Z F; WEN, J G

PRIORITY-DATA: 2001US-292486P (May 21, 2001), 2002US-0151382 (May 21, 2002)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN
WO 200295097 A1	November 28, 2002	E	050	D01F 009/12
US 20030004058 A1	January 2, 2003	N/A	000	D01F 009/12

INT-CL (IPC): B01J023/00, D01F009/12

ABSTRACTED-PUB-NO: WO 200295097A

BASIC-ABSTRACT:

NOVELTY - Non-aligned carbon nanotubes in a reaction vessel are prepared by utilizing catalyst material in the form of catalytic particles. The catalyst material comprises a catalyst substrate material.

DETAILED DESCRIPTION - Preparation of non-aligned carbon nanotubes (CNT) reaction vessel involves:

(i) providing in a reactor, a catalyst material in the form of catalytic particles;



US 20030004058A1

(19) United States  
(12) Patent Application Publication (10) Pub. No.: US 2003/0004058 A1  
Li et al. (43) Pub. Date: Jan. 2, 2003

(54) VARIED MORPHOLOGY CARBON NANOTUBES AND METHOD FOR THEIR MANUFACTURE  
(50) Provisional application No. 60/292,486, filed on May 21, 2001.

(75) Inventors: Wenzhi Li, Brookline, MA (US); Jian Guo Wen, Champaign, IL (US); Zhi Feng Ren, Rosindale, MA (US)  
(51) Int. Cl.<sup>7</sup> D01F 9/12  
(52) U.S. Cl. 902/258; 423/447.3

Correspondence Address:  
PALMER & DODGE, LLP  
PAULA CAMPBELL EVANS  
111 HUNTINGTON AVENUE  
BOSTON, MA 02199 (US)

(73) Assignee: Trustees of Boston College  
(21) Appl. No.: 10151,382  
(22) Filed: May 20, 2002

(57) ABSTRACT  
The present invention describes the preparation of carbon nanotubes of varied morphology, catalyst materials for their synthesis. The present invention also describes reactor apparatus and methods of operating and controlling process parameters for the manufacture carbon nanotubes with predetermined morphologies in relatively high purity and in high yields. In particular, the present invention provides methods for the preparation of non-aligned carbon nanotubes with controllable morphologies, catalyst materials and methods for their manufacture.

Document ID	Title
WO 163028 A1	METHOD FOR OBTAINING
WO 200295097 A	Preparation of non-aligned car
US 20020046872 A	Composition of matter used in
WO 200130694 A	Aligning single-wall carbon n

DERWENT-ACC-NO: 2002-425636

DERWENT-WEEK: 200336

Times New Roman 12 TION LTD

**TITLE:** Composition of matter used in antennas, electromagnetic and electro-optic devices, comprises single-wall carbon nanotube partially coated with polymer molecule(s)

**INVENTOR:** COLBERT, D T; O'CONNELL, M; SMALLEY, R E; SMITH, K A

**PRIORITY-DATA:** 2001US-268269P (February 13, 2001), 2000US-227604P (Aug 2000), 2001US-0935994 (August 23, 2001), 2001US-0935493 (August 23, 2001), 2001US-0935995 (August 23, 2001)

**PATENT-FAMILY:**

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN
EP 1313900 A2	May 28, 2003	E	000	D01F 009/12
WO 200216257 A2	February 28, 2002	E	039	C01B 000/00
US 20020046872 A1	April 25, 2002	N/A	000	H01B 017/60
US 20020048632 A1	April 25, 2002	N/A	000	D01F 009/12
US 20020068170 A1	June 6, 2002	N/A	000	B32B 005/16
AU 200186655 A	March 4, 2002	N/A	000	C01B 000/00

**INT-CL (IPC):** B05D001/28, B05D003/02, B05D007/22, B32B005/16, B32B009/00, B67B007/00, C01B000/00, C01B031/00, C09C001/56, D01F009/12, D02G003/00, G01F011/00, H01B017/60

**ABSTRACTED-PUB-NO:** US20020046872A

**BASIC-ABSTRACT:**

**NOVELTY -** The composition of matter comprises single-wall carbon nanotube



US 20020046872A1

(19) United States

(12) Patent Application Publication  
Smalley et al.

(10) Pub. No.: US 2002/0046872 A1  
(43) Pub. Date: Apr. 25, 2002

(54) POLYMER-WRAPPED SINGLE WALL CARBON NANOTUBES

(52) U.S. CL. 174/137 A

(76) Inventors: Richard E. Smalley, Houston, TX (US); Daniel T. Colbert, Houston, TX (US); Ken A. Smith, Katy, TX (US); Michael O'Connell, Pearland, TX (US)

(37) ABSTRACT

Correspondence Address:  
Winstead Sechrest & Minick P.C.  
1400 Renaissance Tower  
Dallas, TX 75276-2199 (US)

(21) Appl. No.: 09/935,994

(22) Filed: Aug. 23, 2001

Related U.S. Application Data

(65) Non-provisional of provisional application No. 60/227,604, filed on Aug. 24, 2000. Non-provisional of provisional application No. 60/248,369, filed on Feb. 13, 2001.

Publication Classification

(51) Int. Cl. H01B 17/60

The present invention relates to new compositions of matter and articles of manufacture comprising SWNTs as nanometer scale conducting rods dispersed in an electrically-insulating matrix. These compositions of matter have novel and useful electrical, mechanical, and chemical properties including applications in antennas, electromagnetic and electro-optic devices, and high-strength materials. Other compositions of matter and articles of manufacture are disclosed, including polymer-coated and polymer wrapped single-wall nanotubes (SWNTs), small ropes of polymer-coated and polymer-wrapped SWNTs and materials comprising same. This composition provides one embodiment of the SWNT conducting-rod composite mentioned above, and also enables creation of high-concentration suspensions of SWNTs and compatibilization of SWNTs with polymeric matrices in composite materials. This solubilization and compatibilization, in turn, enables chemical manipulation of SWNT and production of composite fibers, films, and solids comprising SWNTs.



DERWENT-ACC-NO: 2001-451330

DERWENT-WEEK: 200325

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TITLE: Aligning single-wall carbon nano-tubes for making e.g.  
high strength fibers and cables, comprises subjecting to  
magnetic or electric field

INVENTOR: CASAVANT, M J; CHIANG, W ; COLBERT, D T ; HAUGE, R H ;  
HUFFMAN, C B  
; QIN, X C ; SAINI, R K ; SMALLEY, R E ; SMITH, K A ; WALTERS, D A  
; YAKOBSON, B I

PRIORITY-DATA: 1999US-161717P (October 27, 1999)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
JP 2003512286 W	April 2, 2003	N/A	070	C01B 031/02
WO 200130694 A1	May 3, 2001	E	073	C01B 031/02
AU 200122483 A	May 8, 2001	N/A	000	C01B 031/02
EP 1226093 A2	July 31, 2002	E	000	C01B 031/02
CN 1359352 A	July 17, 2002	N/A	000	C01B 031/02
KR 2002047030 A	June 21, 2002	N/A	000	B82B 003/00

INT-CL (IPC): B82B003/00, C01B031/02

ABSTRACTED-PUB-NO: WO 200130694A

BASIC-ABSTRACT:

NOVELTY - Single-wall carbon nanotubes (SWNT) are aligned by subjecting them to  
a magnetic field or an electric field.

DETAILED DESCRIPTION - INDEPENDENT CLAIMS are also included for the  
following:

(A) a method of assembling field-**aligned** SWNT into three-dimensional structure in which the tubes are **parallel** to each other;

(B) a material comprising **aligned** single-wall nanotubes;

(C) a method of creating objects and materials from field-**aligned** tubes in solution or **suspension**, comprising modifying the solvent strength of the nano-tube solution to precipitate tubes;

(D) a method of forming a membrane of **aligned** SWNT, comprising field-**aligning** end-derivatized SWNT, and diffusing and chemically attaching the SWNT to a substrate oriented **perpendicular** to the field-alignment direction;

(E) an apparatus for forming **arrays of aligned** SWNT, comprising a tank, a positive electrode disposed in the tank, a negative electrode disposed in the tank, a filter disposed in the tank near the positive electrode, SWNT suspended in a solution within a tank, and a source of magnetic field for **aligning** the SWNT; and

(F) a method of post-processing macroscopic ordered nano-tube assemblies to selectively enhance material properties.

USE - Used for **aligning** single-wall **carbon nano-tubes**. It can be employed to produce macroscopic assembly of single-wall **carbon nanotubes**, which can be utilized for electrical, chemical, mechanical, and biological applications. It can be utilized to form materials that can be used for high strength fibers and cables, electrical transmission lines, structural materials, impact-resistant materials, armor, structural laminates having layers with different tube orientations, pressure vessel exteriors and reinforcement, thermal management materials (e.g., heat-transporting materials), heat-resistant materials, airframe (components) for aircraft and missiles, vehicle bodies, ship hulls, chemically inert materials, electrochemical electrodes, battery electrodes, catalyst supports, biologically-inert materials, sensors, and materials that absorb, support and dispense moieties that intercalate, and transducer elements.

ADVANTAGE - The method allows the single-wall **carbon nano-tubes to be aligned** in the same direction, thus capable of forming macroscopic ordered assembly of **carbon nanotubes** having remarkable physical, electrical, and chemical properties.

----- KWIC -----

Basic Abstract Text - ABTX (1):

NOVELTY - Single-wall carbon nanotubes (SWNT) are aligned by subjecting them to a magnetic field or an electric field.

Basic Abstract Text - ABTX (3):

(A) a method of assembling field-aligned SWNT into three-dimensional structure in which the tubes are parallel to each other;

Basic Abstract Text - ABTX (4):

(B) a material comprising aligned single-wall nanotubes;

Basic Abstract Text - ABTX (5):

(C) a method of creating objects and materials from field-aligned tubes in solution or suspension, comprising modifying the solvent strength of the nano-tube solution to precipitate tubes;

Basic Abstract Text - ABTX (6):

(D) a method of forming a membrane of aligned SWNT, comprising field-aligning end-derivatized SWNT, and diffusing and chemically attaching the SWNT to a substrate oriented perpendicular to the field-alignment direction;

Basic Abstract Text - ABTX (7):

(E) an apparatus for forming arrays of aligned SWNT, comprising a tank, a positive electrode disposed in the tank, a negative electrode disposed in the tank, a filter disposed in the tank near the positive electrode, SWNT suspended in a solution within a tank, and a source of magnetic field for aligning the SWNT; and

Basic Abstract Text - ABTX (9):

USE - Used for aligning single-wall carbon nano-tubes. It can be employed to produce macroscopic assembly of single-wall carbon nanotubes, which can be utilized for electrical, chemical, mechanical, and biological applications. It can be utilized to form materials that can be used for high strength fibers and cables, electrical transmission lines, structural materials, impact-resistant materials, armor, structural laminates having layers with different tube

orientations, pressure vessel exteriors and reinforcement, thermal management materials (e.g., heat-transporting materials), heat-resistant materials, airframe (components) for aircraft and missiles, vehicle bodies, ship hulls, chemically inert materials, electrochemical electrodes, battery electrodes, catalyst supports, biologically-inert materials, sensors, and materials that absorb, support and dispense moieties that intercalate, and transducer elements.

Basic Abstract Text - ABTX (10):

ADVANTAGE - The method allows the single-wall carbon nano-tubes to be aligned in the same direction, thus capable of forming macroscopic ordered assembly of carbon nanotubes having remarkable physical, electrical, and chemical properties.

Title - TIX (1):

Aligning single-wall carbon nano-tubes for making e.g. high strength fibers and cables, comprises subjecting to magnetic or electric field

Standard Title Terms - TTX (1):

ALIGN SINGLE WALL CARBON NANO TUBE HIGH STRENGTH FIBRE  
CABLE COMPRISE  
SUBJECT MAGNETIC ELECTRIC FIELD

Document ID	Title
US 20030077515 A1	Conducting polymer-carbon na
US 20030039604 A1	Modification of nanotubes oxi
US 20020172639 A1	Carbon nanotube structures, ca
US 20020150529 A1	Single-wall carbon nanotubes

DOCUMENT-IDENTIFIER: US 20020172639 A1

TITLE: Carbon nanotube structures, carbon nanotube devices using the same and method for manufacturing carbon

Times New Roman 12

----- KWIC -----

#### Abstract Paragraph - ABTX (1):

Carbon nanotube structures are provided, in which the networks with a desired area and volume, where the carbon nanotubes are electrically or magnetically connected, are formed and the method for easily manufacturing the carbon nanotube structures with less carbon nanotube structures. Carbon nanotube devices are also provided, to which the useful carbon nanotube structures mentioned above are applied. A method for manufacturing carbon nanotube structures includes the steps of applying carbon nanotubes to a low-viscosity dispersion medium to obtain a high-viscosity dispersing liquid which includes carbon nanotubes, and forming a network of the carbon nanotubes having electrical and/or magnetic connections therebetween by removing the low-viscosity dispersion medium from the high-viscosity dispersed liquid.

#### Title - TTL (1):

Carbon nanotube structures, carbon nanotube devices using the same and method for manufacturing carbon nanotube structures

#### Summary of Invention Paragraph - BSTX (8):

[0007] Apart from this, the carbon nanotubes discovered recently are made of a tubular material with a thickness of 1 μm or smaller (in diameter). Ideally, a carbon face of a hexagon mesh forms a tube in parallel to an axis of the tube and plural tubes may be formed. It is theoretically estimated that the carbon nanotubes have either a metallic or semiconductor property depending on how carbon hexagon meshes are linked and the thickness of the tubes,



US 20020172639 A1

(19) United States

(12) Patent Application Publication  
Horuchi et al.

(10) Pub. No.: US 2002/0172639 A1  
(43) Pub. Date: Nov. 21, 2002

(54) CARBON NANOTUBE STRUCTURES,  
CARBON NANOTUBE DEVICES USING THE  
SAME AND METHOD FOR  
MANUFACTURING CARBON NANOTUBE  
STRUCTURES

Publication Classification

(51) Int. Cl.<sup>7</sup> B01F 3/12  
(52) U.S. Cl. 423/447.2; 423/447.1

(73) Inventors: Kazuhiro Horuchi,  
Mitsumasa Higashi (JP); Masahiko  
Shimizu, Nobuo Mochi (JP); Hisao  
Yoshizawa, Mitsumasa Higashi (JP)

(57) ABSTRACT

Correspondence Address:  
OLIFF & BERRIDGE, PLC  
P.O. BOX 19928  
ALEXANDRIA, VA 22320 (US)

Carbon nanotube structures are provided, in which the networks with a desired area and volume, where the carbon nanotubes are electrically or magnetically connected, are formed and the method for easily manufacturing the carbon nanotube structures with less carbon nanotube structures. Carbon nanotube devices are also provided, to which the useful carbon nanotube structures mentioned above are applied. A method for manufacturing carbon nanotube structures includes the steps of applying carbon nanotubes to a low-viscosity dispersion medium to obtain a high-viscosity dispersing liquid which includes carbon nanotubes, and forming a network of the carbon nanotubes having electrical and/or magnetic connections therebetween by removing the low-viscosity dispersion medium from the high-viscosity dispersed liquid.

(73) Assignee: FUJI XEROX CO., LTD., Tokyo (JP)

(21) Appl. No.: 10/014,560

(22) Filed: Dec. 14, 2001

(30) Foreign Application Priority Data  
May 21, 2001 (JP) 2001-150804

	Document ID	Title
5	US 20030039604 A1	Modification of nanotubes oxi
6	US 20020172639 A1	Carbon nanotube structures, co
7	US 20020150529 A1	Single-wall carbon nanotubes
8	US 20020130353 A1	Nanoscope wire-based devic

DOCUMENT-IDENTIFIER: US 20020150529 A1

TITLE: Single-wall carbon nanotubes for hydrogen storage or  
superbundle formation



## Abstract Paragraph - ABTX (1):

A method of processing single-walled carbon nanotubes (SWNTs) in the formation of superbundles or for use in hydrogen storage, or both, is provided comprising the steps of mixing a SWNT substrate in a solvent solution into a suspension, and agitating the suspension using an ultrasonic energy means.

## Title - TTL (1):

Single-wall carbon nanotubes for hydrogen storage or superbundle formation

## Summary of Invention Paragraph - BSTX (13):

[0010] Briefly, the invention provides a method of processing single-walled carbon nanotubes (SWNTs) in the formation of superbundles or for use in hydrogen storage, or both, comprising the steps of mixing a SWNT substrate in a solvent solution into a suspension, and agitating the suspension using an ultrasonic energy means.

## Detail Description Paragraph - DETX (12):

[0042] Conclusively, the 16 h 3M HNO<sub>3</sub> reflux decreases the domain size of the disordered carbon and produces a uniform carbon coating on the SWNTs without damaging them. Our own temperature programmed desorption studies show that the nitric acid reflux introduces reactive functional groups onto the surfaces of the non-nanotube carbon material. These two effects serve to maximize the surface area of the nonnanotube carbon and provide for enhanced oxidation kinetics. Furthermore, since the functionalized coating is oxidized



US 20020150529 A1

(19) United States

(12) Patent Application Publication

Dillon et al.

(10) Pub. No.: US 2002/0150529 A1

(43) Pub. Date: Oct. 17, 2002

(54) SINGLE-WALL CARBON NANOTUBES FOR  
HYDROGEN STORAGE OR SUPERBUNDLE  
FORMATION

## Related U.S. Application Data

(50) Provisional application No. 60/177,075, filed on Jan.  
19, 2000.

(76) Inventors: Anne C. Dillon, Boulder, CO (US);  
Thomas Gennett, Pitsford, NY (US);  
Michael J. Heben, Denver, CO (US)

## Publication Classification

(51) Int. Cl.<sup>7</sup> D01F 9/12  
(52) U.S. Cl. 422/460

## Correspondence Address:

Paul J. White  
Senior Counsel  
National Renewable Energy Laboratory  
1617 Cole Boulevard  
Golden, CO 80401 (US)

## (57) ABSTRACT

(21) Appl. No.: 10/110,082

(22) PCT Filed: Jan. 17, 2001

(86) PCT No.: PCT/US01/01698

A method of processing single-walled carbon nanotubes (SWNTs) in the formation of superbundles or for use in hydrogen storage, or both, is provided comprising the steps of mixing a SWNT substrate in a solvent solution into a suspension, and agitating the suspension using an ultrasonic energy means.

DOCUMENT-IDENTIFIER: US 20020122765 A1

TITLE: Carbon nanotube structures and method for manufacturing the same

----- KWIC -----

Abstract Paragraph - ABTX (1):

Carbon nanotube structures which enhances handling of carbon nanotubes, enabling them to be applied in a wide variety fields such as electronic devices, functional materials, and structural materials containing carbon nanotubes, and a method for producing them are provided. A method for manufacturing carbon nanotube structures includes the step of forming liquid bridges of a liquid at gaps among plural objects and/or at plural gaps among portions of an object. The plural carbon nanotubes are dispersed in the liquid and linked together, then arranged structurally to the liquid bridges, and the carbon nanotube structures are manufactured in this way.

Title - TTL (1):

Carbon nanotube structures and method for manufacturing the same

Summary of Invention Paragraph - BSTX (8):

[0007] Apart from this, the carbon nanotubes discovered recently are made of a tubular material with a thickness of 1 .mu.m smaller (in diameter). Ideally, a carbon face of a hexagon mesh forms a tube in parallel to an axis of the tube and multiple tubes may be formed. It may be theoretically estimated that the carbon nanotubes have either metallic or semiconductor property depending on how carbon hexagon meshes are linked and the thickness of the tubes, allowing expectation that it will be a promising functional material.

Summary of Invention Paragraph - BSTX (11):

[0010] Finer than carbon fibers, the material with 1 .mu.m or smaller of diameter is generally called a carbon nanotube and distinguished from the carbon fiber, although no clear line can be run between both the types of carbon fibers. By a narrow definition, the material, of which carbon faces with hexagon meshes are almost parallel to the axis of the tube, is called a

carbon nanotube and even a variant of the carbon nanotube, around which amorphous carbon and metal catalyst surrounds, is included in the carbon nanotube. (Note that with respect to the present invention, this narrow definition is applied to the carbon nanotube.)

Summary of Invention Paragraph - BSTX (13):

[0012] The carbon fibers have larger diameters and incomplete cylindrical mesh structures **parallel** to the axes of the tubes. The carbon nanotubes produced by a vapor-phase pyrolysis method using a catalyst have a tubular mesh structure **parallel** to the axis of the tube in the vicinity of a center of the tube and in many cases, a large amount of carbon having a disordered structure surrounds it.

Summary of Invention Paragraph - BSTX (29):

[0028] With respect to a shape of the resultant carbon nanotube, its diameter is about 3.5 to 75 nm and length is 5 to 1000 times the diameter. A mesh structure of carbon is **parallel** to an axis of the tube with less pyrolytic carbon adhered to an outer wall of the tube.

Summary of Invention Paragraph - BSTX (32):

[0031] The arc discharge method, which was first discovered by Iijima, is described in detail in Nature, Vol. 354, 1991, p 56 to 58. The arc discharge method is a simple method, by which direct current arc discharge is performed using carbon electrode rods in an atmosphere containing argon under about 13300 Pa (100 Torr). The carbon nanotubes grow with 5 to 20 nm of carbon particles in partial area on a surface of a negative electrode. The resultant carbon nanotubes have a layer structure, in which tubular carbon meshes with 4 to 30 nm of diameter and about 1 to 50 .mu.m of length are overlapped; the mesh structure of carbon being helically formed in **parallel** with its axis.

Detail Description Paragraph - DETX (37):

[0101] The functional particles include metal particles, for example, gold, metal oxide particles such as ZnO.sub.2 and TiO.sub.2, inter-metallic compound particles made of an alloy, and vecicle, ceramics, fullerene, derivatives of fullerene, polymer particles, micellar structures in a liquid, **colloidal** particles, and lipid, and depending on its application, compounds of the particles or the treated particles can be used.

Detail Description Paragraph - DETX (42):

[0106] For the bridging function to be implemented, any of the atoms, molecules, ions, particle, and fibers with two or more portions having such a characteristic that it is difficult to separate after they have got contact with the carbon nanotubes may be used. It is preferable that the carbon nanotubes themselves are pre-treated. For example, after the carbon nanotubes have been treated with a strong acid solution, they have carbonyl groups (COOH) and in this case, bridging between the carbon nanotubes is easily achieved by the molecules containing functional groups such as hydroxyl groups (OH), amino acid (NH.sub.2), and thiol group (SH), which are prone to react with the carbonyl group.

Detail Description Paragraph - DETX (43):

[0107] The carbon nanotubes containing water-soluble functional groups such as carbonyl groups can be ionized in a water solution to achieve the bridged structures using multivalent ions. For example, in the state that carboxylic acid is ionized (COO.sup.-), calcium ions (Ca.sup.2+), magnesium ions (Mg.sup.2+), and aluminum ions (Al.sup.3+) can be used.

Detail Description Paragraph - DETX (55):

[0119] In the case of FIG. 10A, since the amount of the liquid 2 with the carbon nanotubes (not indicated in the figure) dispersed is small, only fine liquid bridges a11 are formed at the gaps among cubes 18, at which the carbon nanotubes gather and are linked together and structured. At this time, the liquid 2 forming the liquid bridges a11 reached the board 12, which means that the liquid bridges a11 are formed not only at the gaps among the cubes 18 each other but also at the gaps between them and the board 12. For this example, for example, by evaporating the liquid 2 and removing the cubes 18 as required, three carbon nanotube structures linking linearly and parallel to each other can be formed on the surface of the board 12 at the same time, which allows wiring with a shape mentioned above to be achieved. Alternately, they can be used as three electric elements, in which the characteristics of the carbon nanotubes are applied. In addition, as mentioned above, by structuring the carbon nanotubes together with the other objects, the carbon nanotube structures having various characteristics corresponding to those of the other objects to be added can be achieved.

Detail Description Paragraph - DETX (61):

[0125] At the liquid bridges a13 formed in FIG., 11A, the carbon nanotubes link to be structured. In this way, the carbon nanotube structures are formed

at the contacts between the plate member 20b or the vertical part 20c" and the plate element 20a or the flat bottom 20c'. For this example, for example, by evaporating the liquid 2 and/or removing the plate element 20b or the vertical part 20c" as required, two carbon nanotube structures linking linearly and **parallel** to one another can be formed at the same time, which allows wiring with shape mentioned above on the surface of the plate element 20a (or/and the plate element 20b) or the plate element 20c". Alternately, they can be used as two electric elements, in which the characteristics of the carbon nanotubes are applied. Note that after the plate element 20b or the vertical part 20c" has been removed, at the linear gaps between two carbon nanotube structures one another, none exist, that is, hollows are formed.

Detail Description Paragraph - DETX (63):

[0127] At the liquid bridges a14 and a14' formed in FIG. 11C, the carbon nanotubes gather and are linked together and structured. In this way, the carbon nanotube structures are formed at the contacts between the plate member 20b or the vertical part 20c" and the plate element 20a or the flat bottom 20d'. For this example, for instance, by evaporating the liquid 2 and/or removing the plate element 20b or the vertical part 20d" as required, six carbon nanotube structures linking linearly and **parallel** to each other can be formed at the same time, which allows wiring with shape mentioned above on the surface of the plate element 20a (or/and the plate element 20b) or the surface of the plate element 20d. Alternately, they can be used as six electric elements, in which the characteristics of the carbon nanotubes are applied. Note that after the plate element 20b or the vertical part 20d" has been removed, at the linear gaps among six carbon nanotube structures each other, none exist, that is, hollows are formed

Detail Description Paragraph - DETX (145):

[0209] The pH value and ion concentration in the dispersing liquid are factors, which govern an electrical attraction-repulsion balance in the dispersing liquid, have significant effects on the stability of the surface-active agent in the dispersing liquid, the dispersibility of the carbon nanotubes being strongly affected. Moreover, since the **carbon nanotubes** themselves treated with the solutions such as a strong acid solution are prone to dissolve, although a dispersing agent does not always have to be used, special care should be taken in applying it to find out the optimal conditions because the added **functional group** would strongly affect the pH value and ion concentration.

Detail Description Paragraph - DETX (147):

[0211] It is desirable that for the dispersing liquid with the multiple fine particles (if necessary, any other object) dispersed, the particles are fully dispersed, although it may be so much desirable as for the dispersing liquid with the carbon nanotubes dispersed. The parameters including physical forces such as ultrasonic, a pH value of the solution, addition of dispersing agents such as a surface-active agent, and temperature should be set to gain moderate dispersibility. Concretely, it is preferable that they are kept in the dispersion state called "**colloidal**" and such a dispersing agent is selected that mixture of it with the dispersing liquid of carbon nanotubes does not break the stable state. To enhance dispersibility, the method for increasing the viscosity of the carbon nanotubes can be selected. However, to mix the carbon nanotubes and the dispersing agent more quickly, the viscosity is preferably set to a lower value.

Detail Description Paragraph - DETX (163):

[0225] c) Water solution (**colloidal** solution) with 3 mass % of latex particles (polystyrene, average diameter of particle 0.3  $\mu\text{m}$ , spherical) .  
... 1.0 g

Detail Description Paragraph - DETX (167):

[0229] By mixing and stirring the dispersing liquid with the carbon nanotubes dispersed prepared in (Process 1) and the dispersing liquid (**colloidal** solution) with 1.0 g of latex particles dispersed, the dispersing liquid with the carbon nanotubes and latex particles dispersed is prepared. The resulting dispersing liquid has 75 mN/m of surface tension.

Detail Description Paragraph - DETX (175):

[0236] c) Water solution (**colloidal** solution) with 3 mass % of latex particles (polystyrene, average diameter of particle 0.3  $\mu\text{m}$ , spherical) .  
... 1.0 g

Detail Description Paragraph - DETX (179):

[0240] By mixing and stirring the dispersing liquid with the carbon nanotubes dispersed prepared in (Process 1) and the solution (**colloidal** solution) with 1.0 g of latex particles dispersed prepared in c), the dispersing liquid with the carbon nanotubes and latex particles dispersed is prepared. The resulting dispersing liquid has 80 mN/m of surface tension.

Detail Description Paragraph - DETX (187):

[0247] c) Water solution (**colloidal** solution) with 3 mass % of latex particles (polyethylene, average diameter of particle 0.3  $\mu\text{m}$ , spherical) .  
.. 1.0 g

Detail Description Paragraph - DETX (191):

[0251] By mixing and stirring the dispersing liquid with the carbon nanotubes dispersed prepared in (Process 1) and the solution (**colloidal** solution) with 1.0 g of latex particles dispersed, the dispersing liquid with the carbon nanotubes and latex particles dispersed is prepared. The resulting dispersing liquid had Pa.s of surface tension.

L Number	Hits	Search Text	DB	Time stamp
1	1626	((carbon or graphite) with (swnt or nano-tube or nanotube or nano-tubing or nanotubing or nano\$1tubule or (nano adj1 (tube or tubing or tubule))))	EPO; JPO; DERWENT	2003/10/01 09:43
2	321616	(suspension or colloid or sol or colloidal or sol-gel)	EPO; JPO; DERWENT	2003/10/01 09:43
3	40	((carbon or graphite) with (swnt or nano-tube or nanotube or nano-tubing or nanotubing or nano\$1tubule or (nano adj1 (tube or tubing or tubule)))) and ((suspension or colloid or sol or colloidal or sol-gel) )	EPO; JPO; DERWENT	2003/10/01 09:34
4	5	(align or aligned or aligning or parallelize or parallel or parallelizing or array or perpendicular) and (((carbon or graphite) with (swnt or nano-tube or nanotube or nano-tubing or nanotubing or nano\$1tubule or (nano adj1 (tube or tubing or tubule)))) and ((suspension or colloid or sol or colloidal or sol-gel) )	EPO; JPO; DERWENT	2003/10/01 09:44
5	422	((carbon or graphite) with (swnt or nano-tube or nanotube or nano-tubing or nanotubing or nano\$1tubule or (nano adj1 (tube or tubing or tubule))))ti,ab.	USPAT; US-PGPUB	2003/10/01 09:45
6	139544	(chemical or chemically) near2 (treatment or treat or treated or treating) or functionalize or functionalizing or functionalized or functional-group or (functional adj1 group)	USPAT; US-PGPUB	2003/10/01 09:43
7	1707	((carbon or graphite) with (swnt or nano-tube or nanotube or nano-tubing or nanotubing or nano\$1tubule or (nano adj1 (tube or tubing or tubule))))	USPAT; US-PGPUB	2003/10/01 09:43
8	64	((chemical or chemically) near2 (treatment or treat or treated or treating) or functionalize or functionalizing or functionalized or functional-group or (functional adj1 group)) with (((carbon or graphite) with (swnt or nano-tube or nanotube or nano-tubing or nanotubing or nano\$1tubule or (nano adj1 (tube or tubing or tubule))))	USPAT; US-PGPUB	2003/10/01 09:43
9	418798	(suspension or colloid or sol or colloidal or sol-gel)	USPAT; US-PGPUB	2003/10/01 09:44
10	35	((chemical or chemically) near2 (treatment or treat or treated or treating) or functionalize or functionalizing or functionalized or functional-group or (functional adj1 group)) with (((carbon or graphite) with (swnt or nano-tube or nanotube or nano-tubing or nanotubing or nano\$1tubule or (nano adj1 (tube or tubing or tubule)))) and ((suspension or colloid or sol or colloidal or sol-gel) )	USPAT; US-PGPUB	2003/10/01 09:44
11	23	(align or aligned or aligning or parallelize or parallel or parallelizing or array or perpendicular) and (((chemical or chemically) near2 (treatment or treat or treated or treating) or functionalize or functionalizing or functionalized or functional-group or (functional adj1 group)) with (((carbon or graphite) with (swnt or nano-tube or nanotube or nano-tubing or nanotubing or nano\$1tubule or (nano adj1 (tube or tubing or tubule)))) and ((suspension or colloid or sol or colloidal or sol-gel) )	USPAT; US-PGPUB	2003/10/01 09:45
12	11	((carbon or graphite) with (swnt or nano-tube or nanotube or nano-tubing or nanotubing or nano\$1tubule or (nano adj1 (tube or tubing or tubule))))ti,ab.) and ((align or aligned or aligning or parallelize or parallel or parallelizing or array or perpendicular) and (((chemical or chemically) near2 (treatment or treat or treated or treating) or functionalize or functionalizing or functionalized or functional-group or (functional adj1 group)) with (((carbon or graphite) with (swnt or nano-tube or nanotube or nano-tubing or nanotubing or nano\$1tubule or (nano adj1 (tube or tubing or tubule)))) and ((suspension or colloid or sol or colloidal or sol-gel) )))	USPAT; US-PGPUB	2003/10/01 09:45

Document ID	Title
1 US 20030133865 A1	Single-wall carbon nanotube
2 US 20030102222 A1	Deposition method for nanos
3 US 20030090190 A1	Field emission devices using
4 US 20030089899 A1	Nanoscale wires and related c

DOCUMENT-IDENTIFIER: US 20030133865 A1

TITLE: Single-wall carbon nanotube alewives, process for making, and compositions thereof

Times New Roman 12

#### Summary of Invention Paragraph - BSTX (7):

[0010] The ability to disperse single-wall carbon nanotubes remains one of the largest barriers in realizing the full potential of single-wall carbon nanotubes in various applications. Besides the challenge of dispersing single-wall carbon nanotubes, even when dispersed, the single-wall carbon nanotubes and ropes of single wall carbon nanotubes may not provide the optimum configuration to achieve the full potential of the strength and properties of the nanotubes unless they are aligned. Controlled alignment of single-wall carbon nanotubes from surfactant-assisted suspensions and fabrication of macroscopic forms of single-wall carbon nanotubes such as fibers or shear-aligned aggregates face the inherent limitations of the single-wall carbon nanotube-surfactant system. Since the van der Waals forces between the single-wall carbon nanotubes and ropes of single-wall carbon nanotubes are larger than the weak electrostatic repulsions arising from the adsorbed surfactant molecules, the single-wall carbon nanotube solutions are generally very low in concentration and impractical for many applications. Although oriented single-wall carbon nanotube fibers could be prepared with surfactant dispersions by shear flow-induced alignment in a co-flowing stream of polymer solution, the single-wall carbon nanotube concentrations attainable in a sodium dodecyl benzene sulfonate/single-wall carbon nanotube/water system are generally too low (i.e., less than about 1 wt %) to achieve coordinated single-wall carbon nanotube alignment.

(19) United States  
(12) Patent Application Publication (10) Pub. No.: US 2003/0133865 A1  
Smalley et al. (43) Pub. Date: Jul. 17, 2003

(54) SINGLE-WALL CARBON NANOTUBE  
ALEWIVES, PROCESS FOR MAKING, AND  
COMPOSITIONS THEREOF

Related U.S. Application Data

(75) Inventors: Richard E. Smalley, Houston, TX (US); Rajesh Kumar Saito, Houston, TX (US); Ramesh Shrivastava, Houston, TX (US); Robert H. Baugh, Houston, TX (US); Virginia A. Davis, Webster, TX (US); Matteo Pasquali, Houston, TX (US); Lars Martin Ericson, Houston, TX (US); Saito, Kumar, Lawrenceville, GA (US); Sreekumar Thalliyil Veedu, Atlanta, GA (US)

(50) Provisional application No. 60/203,469, filed on Jul. 6, 2001. Provisional application No. 60/303,470, filed on Jul. 4, 2001. Provisional application No. 60/337,561, filed on Nov. 8, 2001. Provisional application No. 60/337,551, filed on Dec. 7, 2001.

Publication Classification

(51) Int. Cl. D01F 9/12  
(51) U.S. Cl. 423/447.1

(57) ABSTRACT

The present invention involves alewives of highly aligned single-wall carbon nanotubes (SWNT), process for making the same and compositions thereof. The present invention provides a method for effectively making carbon alewives, which are discrete, acicular-shaped aggregates of aligned single-wall carbon nanotubes and resemble the Atlantic fish of the same name. Single-wall carbon nanotube alewives can be conveniently dispersed in materials such as polymers, ceramics, metals, metal oxides and liquids. The process for preparing the alewives comprises mixing single-wall carbon nanotubes with 100% sulfuric acid or a superacid, heating and stirring, and slowly introducing water into the single-wall carbon nanotube/acid mixture to form the alewives. The alewives can be recovered, washed and dried. The properties of the single-wall carbon nanotubes are retained in the alewives.

Correspondence Address:  
Rosa Spencer Garson  
Winstead Sechrest & Minick P.C.  
3400 Renaissance Tower  
1281 Main Street  
Dallas, TX 75226 (US)

(73) Assignee: William Marsh Rice University, Houston, TX (US)

(21) Appl. No.: 10/787,929

(22) Filed: Jul. 2, 2002



DOCUMENT-IDENTIFIER: US 20020159943 A1

TITLE: Method for forming an array of single-wall carbon nanotubes and compositions thereof

----- KWIC -----

Abstract Paragraph - ABTX (1):

A method for purifying a mixture comprising single-wall carbon nanotubes and amorphous carbon contaminate is disclosed. The method includes the steps of heating the mixture under oxidizing conditions sufficient to remove the amorphous carbon, followed by recovering a product comprising at least about 80% by weight of single-wall carbon nanotubes. A method for producing tubular carbon molecules of about 5 to 500 nm in length is also disclosed. The method includes the steps of cutting single-wall nanotube containing-material to form a mixture of tubular carbon molecules having lengths in the range of 5-500 nm and isolating a fraction of the molecules having substantially equal lengths. The nanotubes may be used, singularly or in multiples, in power transmission cables, in solar cells, in batteries, as antennas, as molecular electronics, as probes and manipulators, and in composites.

Title - TTL (1):

Method for forming an array of single-wall carbon nanotubes and compositions thereof

Summary of Invention Paragraph - BSTX (6):

[0005] An improved method of producing single-wall nanotubes is described in U.S. Ser. No. 08/687,665, entitled "Ropes of Single-Walled Carbon Nanotubes" incorporated herein by reference in its entirety. This method uses, inter alia, laser vaporization of a graphite substrate doped with transition metal atoms, preferably nickel, cobalt, or a mixture thereof, to produce single-wall carbon nanotubes in yields of at least 50% of the condensed carbon. The single-wall nanotubes produced by this method tend to be formed in clusters, termed "ropes," of 10 to 1000 single-wall carbon nanotubes in parallel alignment, held together by van der Waals forces in a closely packed triangular lattice. Nanotubes produced by this method vary in structure, although one structure tends to predominate.

Summary of Invention Paragraph - BSTX (11):

[0009] It is also an object of this invention to provide a molecular array of purified single-wall carbon nanotubes for use as a template in continuous growing of macroscopic carbon fiber.

Summary of Invention Paragraph - BSTX (13):

[0011] It is also an object of the present invention to provide a new class of tubular carbon molecules, optionally derivatized with one or more functional groups, which are substantially free of amorphous carbon.

Summary of Invention Paragraph - BSTX (14):

[0012] It is also an object of this invention to provide a number of devices employing the, carbon fibers,, nanotube molecular arrays and tubular carbon molecules of this invention.

Summary of Invention Paragraph - BSTX (19):

[0017] In another embodiment, a method for forming a macroscopic molecular array of tubular carbon molecules is disclosed. This method includes the steps of providing at least about 10.sup.6 tubular carbon molecules of substantially similar length in the range of 50 to 500 nm; introducing a linking moiety onto at least one end of the tubular carbon molecules; providing a substrate coated with a material to which the linking moiety will attach; and contacting the tubular carbon molecules containing a linking moiety with the substrate.

Summary of Invention Paragraph - BSTX (20):

[0018] In another embodiment, another method for forming a macroscopic molecular array of tubular carbon molecules is disclosed. First, a nanoscale array of microwells is provided on a substrate. Next, a metal catalyst is deposited in each microwells. Next, a stream of hydrocarbon or CO feedstock gas is directed at the substrate under conditions that effect growth of single-wall carbon nanotubes from each microwell.

Summary of Invention Paragraph - BSTX (21):

[0019] In another embodiment, still another method for forming a macroscopic molecular array of tubular carbon molecules is disclosed. It includes the steps of providing surface containing purified but entangled and relatively

endless single-wall carbon nanotube material; subjecting the surface to oxidizing conditions sufficient to cause short lengths of broken nanotubes to protrude up from the surface; and applying an electric field to the surface to cause the nanotubes protruding from the surface to align in an orientation generally perpendicular to the surface and coalesce into an array by van der Waals interaction forces.

Summary of Invention Paragraph - BSTX (22):

[0020] In another embodiment, a method for continuously growing a macroscopic carbon fiber comprising at least about 10.sup.6 single-wall nanotubes in generally parallel orientation is disclosed. In this method, a macroscopic molecular array of at least about 10.sup.6 tubular carbon molecules in generally parallel orientation and having substantially similar lengths in the range of from about 50 to about 500 nanometers is provided. The hemispheric fullerene cap is removed from the upper ends of the tubular carbon molecules in the array. The upper ends of the tubular carbon molecules in the array are then contacted with a catalytic metal. A gaseous source of carbon is supplied to the end of the array while localized energy is applied to the end of the array in order to heat the end to a temperature in the range of about 500.degree. C. to about 1300.degree. C. The growing carbon fiber is continuously recovered.

Summary of Invention Paragraph - BSTX (23):

[0021] In another embodiment, a macroscopic molecular array comprising at least about 10.sup.6 single-wall carbon nanotubes in generally parallel orientation and having substantially similar lengths in the range of from about 5 to about 500 nanometers is disclosed.

Summary of Invention Paragraph - BSTX (25):

[0023] In still another embodiment, macroscopic carbon fiber comprising at least about 10.sup.6 single-wall carbon nanotubes in generally parallel orientation is disclosed.

Summary of Invention Paragraph - BSTX (26):

[0024] In another embodiment, an apparatus for forming a continuous macroscopic carbon fiber from a macroscopic molecular template array comprising at least about 10.sup.6 single-wall carbon nanotubes having a catalytic metal deposited on the open ends of said nanotubes is disclosed. This apparatus includes a means for locally heating only the open ends of the nanotubes in the

template array in a growth and annealing zone to a temperature in the range of about 500.degree. C. to about 1300.degree. C. It also includes a means for supplying a carbon-containing feedstock gas to the growth and annealing zone immediately adjacent the heated open ends of the nanotubes in the template array. It also includes a means for continuously removing growing carbon fiber from the growth and annealing zone while maintaining the growing open end of the fiber in the growth and annealing zone.

Brief Description of Drawings Paragraph - DRTX (7):

[0034] FIG. 4 is a schematic presentation of a portion of an homogeneous SWNT molecular array according to the present invention.

Brief Description of Drawings Paragraph - DRTX (8):

[0035] FIG. 5 is a schematic representation of an heterogeneous SWNT molecular array according to the present invention.

Brief Description of Drawings Paragraph - DRTX (11):

[0038] FIG. 8 is a composite array according to the present invention.

Brief Description of Drawings Paragraph - DRTX (12):

[0039] FIG. 9 is a composite array according to the present invention.

Brief Description of Drawings Paragraph - DRTX (27):

[0054] FIG. 18A is a graph of field flow fractionation (FFF) of a cut nanotubes suspension.

Detail Description Paragraph - DETX (6):

[0061] In defining carbon nanotubes, it is helpful to use a recognized system of nomenclature. In this application, the carbon nanotube nomenclature described by M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, Science of Fullereness and Carbon Nanotubes, Chap. 19, especially pp. 756-760, (1996), published by Academic Press, 525 B Street, Suite 1900, San Diego, Calif. 92101-4495 or 6277 Sea Harbor Drive, Orlando, Fla. 32877 (ISBN 0-12-221820-5), which is hereby incorporated by reference, will be used. The single wall tubular fullerenes are distinguished from each other by double index (n,m) where n and m are integers that describe how to cut a single strip of hexagonal "chicken-wire" graphite so that it makes the tube perfectly when it is wrapped

onto the surface of a cylinder and the edges are sealed together. When the two indices are the same,  $m=n$ , the resultant tube is said to be of the "arm-chair" (or  $n,n$ ) type, since when the tube is cut **perpendicular** to tube axis, only the sides of the hexagons are exposed and their pattern around the periphery of the tube edge resembles the arm and seat of an arm chair repeated  $n$  times. Arm-chair tubes are a preferred form of single-wall carbon nanotubes since they are metallic, and have extremely high electrical and thermal conductivity. In addition, all single-wall nanotubes have extremely high tensile strength.

Detail Description Paragraph - DETX (8):

[0063] The present invention provides a method for making single-wall carbon nanotubes in which a laser beam vaporizes material from a target comprising, consisting essentially of, or consisting of a mixture of carbon and one or more Group VI or Group VIII transition metals. The vapor from the target forms carbon nanotubes that are predominantly single-wall carbon nanotubes, and of those, the (10, 10) tube is predominant. The method also produces significant amounts of single-wall carbon nanotubes that are arranged as ropes, i.e., the single-wall carbon nanotubes run **parallel** to each other. Again the (10, 10) tube is the predominant tube found in each rope. The laser vaporization method provides several advantages over the arc discharge method of making carbon nanotubes: laser vaporization allows much greater control over the conditions favoring growth of single-wall carbon-nanotubes, the laser vaporization method permits continuous operation, and the laser vaporization method produces single-wall carbon nanotubes in higher yield and of better quality. As described herein, the laser vaporization method may also be used to produce longer carbon nanotubes and longer ropes.

Detail Description Paragraph - DETX (39):

[0094] The product of a typical process for making mixtures containing single-wall carbon nanotubes is a tangled felt which can include deposits of amorphous carbon, graphite, metal compounds (e.g., oxides), spherical fullerenes, catalyst particles (often coated with carbon or fullerenes) and possibly multi-wall carbon nanotubes. The single-wall carbon nanotubes may be aggregated in "ropes" or bundles of essentially **parallel** nanotubes.

Detail Description Paragraph - DETX (47):

[0102] In another embodiment, a slightly basic solution (e.g., pH of approximately 8-12) may also be used in the saponification step. The initial cleaning in 2.6 M  $\text{HNO}_3$  converts amorphous carbon in the raw material to various sizes of linked polycyclic compounds, such as fulvic and humic acids,

as well as larger polycyclic aromatics with various **functional groups** around the periphery, especially the carboxylic acid groups. The base solution ionizes most of the polycyclic compounds, making them more soluble in aqueous solution. In a preferred process, the nanotube containing felts are refluxed in 2-5 M HNO<sub>3</sub> for 6-15 hours at approximately 110-125.degree. C. Purified nanotubes may be filtered and washed with 10 mM NaOH solution on a 3 micron pore size TSTP Isopore filter. Next, the filtered nanotubes polished by stirring them for 30 minutes at 60.degree. C. in a S/N (Sulfuric acid/Nitric acid) solution. In a preferred embodiment, this is a 3:1 by volume mixture of concentrated sulfuric acid and nitric acid. This step removes essentially all the remaining material from the tubes that is produced during the nitric acid treatment.

Detail Description Paragraph - DETX (53):

[0108] The short nanotube pieces can be cut to a length or selected from a range of lengths, that facilitates their intended use. For applications involving the individual tubular molecules per se (e.g., derivatives, nanoscale conductors in quantum devices, i.e., molecular wire), the length can be from just greater than the diameter of the tube up to about 1,000 times the diameter of the tube. Typical tubular molecules will be in the range of from about 5 to 1,000 nanometers or longer. For making template **arrays** useful in growing carbon fibers of SWNT as described below, lengths of from about 50 to 500 nm are preferred.

Detail Description Paragraph - DETX (57):

[0112] Cutting may also be achieved by sonicating a **suspension** of SWNTs in a suitable medium such as liquid or molten hydrocarbons. One such preferred liquid is 1,2-dichloroethane. Any apparatus that produces suitable acoustic energy can be employed. One such apparatus is the Compact Cleaner (One Pint) manufactured by Cole-Parmer, Inc. This model operates at 40 KHz and has an output of 20 W. The sonication cutting process should be continued at a sufficient energy input and for a sufficient time to substantially reduce the lengths of tubes, ropes or cables present in the original **suspension**. Typically times of from about 10 minutes to about 24 hours can be employed depending on the nature of the starting material and degree of length reduction sought.

Detail Description Paragraph - DETX (61):

[0116] The cleaned nanotube material may be cut into 50-500 nm lengths, preferably 100-300 nm lengths, by this process. The resulting pieces may form

a **colloidal suspension** in water when mixed with a surfactant such as Triton X-100.TM. (Aldrich, Milwaukee, Wis.). These sable **suspensions** permit a variety of manipulations such as sorting by length using field flow fractionation, and electrodeposition on graphite followed by AFM imaging.

Detail Description Paragraph - DETX (67):

[0122] The procedures described herein produce tubular molecules that are single-wall nanotubes in which the cylindrical portion is formed from a substantially defect-free sheet of graphene (carbon in the form of attached hexagons) rolled up and joined at the two edges **parallel** to its long axis. The nanotube can have a fullerene cap (e.g., hemispheric) at one end of the cylinder and a similar fullerene cap at the other end. One or both ends can also be open. Prepared as described herein these SWNT molecules are substantially free of amorphous carbon. These purified nanotubes are effectively a whole new class of tubular molecules.

Detail Description Paragraph - DETX (93):

[0148] Molecular **Arrays** of Single-Wall Carbon Nanotubes

Detail Description Paragraph - DETX (94):

[0149] An application of particular interest for a homogeneous population of SWNT molecules is production of a substantially two-dimensional **array** made up of single-walled nanotubes aggregating (e.g., by van der Waals forces) in substantially **parallel** orientation to form a monolayer extending in directions substantially **perpendicular** to the orientation of the individual nanotubes. Such monolayer **arrays** can be formed by conventional techniques employing "self-assembled monolayers" (SAM) or Langmuir-Blodgett films, see Hirsch, pp. 75-76. Such a molecular **array** is illustrated schematically in FIG. 4. In this figure, nanotubes 1 are bound to a substrate 2 having a reactive coating 3 (e.g., gold).

Detail Description Paragraph - DETX (96):

[0151] The configuration of the SWNT molecular **array** may be homogenous or heterogeneous depending on the use to which it will be put. Using SWNT molecules of the same type and structure provides a homogeneous **array** of the type shown in FIG. 4. By using different SWNT molecules, either a random or ordered heterogeneous structure can be produced. An example of an ordered heterogeneous **array** is shown in FIG. 5 where tubes 4 are (n,n), i.e., metallic in structure and tubes 5 are (m,n), i.e., insulating. This configuration can

be achieved by employing successive reactions after removal of previously masked areas of the reactive substrate.

Detail Description Paragraph - DETX (97):

[0152] Arrays containing from 10.sup.3 up to 10.sup.10 and more SWNT molecules in substantially parallel relationships can be used per se as a nanoporous conductive molecular membrane, e.g., for use in batteries such as the lithium ion battery. This membrane can also be used (with or without attachment of a photoactive molecule such as cis-(bisthiacyanato bis (4,4'-dicarboxy-2-2'-bipyridine Ru (II)) to produce a highly efficient photo cell of the type shown in U.S. Pat. No. 5,084,365.

Detail Description Paragraph - DETX (98):

[0153] One preferred use of the SWNT molecular arrays of the present invention is to provide a "seed" or template for growth of macroscopic carbon fiber of single-wall carbon nanotubes as described below. The use of a macroscopic cross section in this template is particularly useful for keeping the live (open) end of the nanotubes exposed to feedstock during growth of the fiber. The template array of this invention can be used as formed on the original substrate, cleaved from its original substrate and used with no substrate (the van der Waals forces will hold it together) or transferred to a second substrate more suitable for the conditions of fiber growth.

Detail Description Paragraph - DETX (99):

[0154] Where the SWNT molecular is to be used as a seed or template for growing macroscopic carbon fiber as described below, the array need not be formed as a substantially two-dimensional array. Any form of array that presents at its upper surface a two-dimensional array can be employed. In the preferred embodiment, the template molecular array is a manipulatable length of macroscopic carbon fiber as produced below.

Detail Description Paragraph - DETX (100):

[0155] Another method for forming a suitable template molecular array involves employing purified bucky paper as the starting material. Upon oxidative treatment of the bucky paper surface (e.g., with O.sub.2/CO.sub.2 at about 500.degree. C.), the sides as well as ends of SWNTs are attacked and many tube and/or rope ends protrude up from the surface of the paper. Disposing the resulting bucky paper in an electric field (e.g., 100 V/cm.sup.2 results in the protruding tubes and or ropes aligning in a direction

substantially perpendicular to the paper surface. These tubes tend to coalesce due to van der Waals forces to form a molecular array.

Detail Description Paragraph - DETX (101):

[0156] Alternatively, a molecular array of SWNTs can be made by "combing" the purified bucky paper starting material. "Combing" involves the use of a sharp microscopic tip such as the silicon pyramid on the cantilever of a scanning force microscope ("SFM") to align the nanotubes. Specifically, combing is the process whereby the tip of an SFM is systematically dipped into, dragged through, and raised up from a section of bucky paper. An entire segment of bucky paper could be combed, for example, by: (i) systematically dipping, dragging, raising and moving forward an SFM tip along a section of the bucky paper, (ii) repeating the sequence in (i) until completion of a row, and (iii) repositioning the tip along another row and repeating (i) and (ii). In a preferred method of combing, the section of bucky paper of interest is combed through as in steps (i)-(iii) above at a certain depth and then the entire process is repeated at another depth. For example, a lithography script can be written and run which could draw twenty lines with 0.5  $\mu\text{m}$  spacing in a  $10 \times 10 \mu\text{m}^2$  square of bucky paper. The script can be run seven times, changing the depth from zero to three  $\mu\text{m}$  in 0.5  $\mu\text{m}$  increments.

Detail Description Paragraph - DETX (102):

[0157] Large arrays (i.e.,  $>10^{16}$  tubes) also can be assembled using nanoprobes by combining smaller arrays or by folding linear collections of tubes and/or ropes over (i.e., one folding of a collection of  $n$  tubes results in a bundle with  $2n$  tubes).

Detail Description Paragraph - DETX (103):

[0158] Macroscopic arrays can also be formed by providing a nanoscale microwell structure (e.g., a  $\text{SiO}_2$  coated silicon wafer with  $>10^{16}$  rectangular 10 nm wide, 10 nm deep wells formed in the surface by electron lithographic techniques). A suitable catalyst metal cluster (or precursor) is deposited in each well and a carbon-containing feedstock is directed towards the array under growth conditions described below to initiate growth of SWNT fibers from the wells. Catalysts in the form of preformed nanoparticles (i.e., a few nanometers in diameter) as described in Dai et al., "Single-Wall Nanotubes Produced by Metal-Catalyzed Disproportionation of Carbon Monoxide," Chem. Phys. Lett. 260 (1996), 471-475 ("Dai") can also be used in the wells. An electric field can be applied to orient the fibers in a direction substantially perpendicular to the wafer surface.

Detail Description Paragraph - DETX (104):

[0159] Growth of Continuous Carbon Fiber from SWNT Molecular Arrays

Detail Description Paragraph - DETX (105):

[0160] The present invention provides methods for growing continuous carbon fiber from SWNT molecular arrays to any desired length. The carbon fiber which comprises an aggregation of substantially parallel carbon nanotubes may be produced according to this invention by growth (elongation) of a suitable seed molecular array. The preferred SWNT molecular array is produced as described above from a SAM of SWNT molecules of substantially uniform length. As used herein, the term "macroscopic carbon fiber" refers to fibers having a diameter large enough to be physically manipulated, typically greater than about 1 micron and preferably greater than about 10 microns.

Detail Description Paragraph - DETX (106):

[0161] The first step in the growth process is to open the growth end of the SWNTs in the molecular. This can be accomplished as described above with an oxidative treatment. Next, a transition metal catalyst is added to the open-ended seed array. The transition metal catalyst can be any transition metal that will cause conversion of the carbon-containing feedstock described below into highly mobile carbon radicals that can rearrange at the growing edge to the favored hexagon structure. Suitable materials include transition metals, and particularly the Group VI or VIII transition metals, i.e., chromium (Cr), molybdenum (Mo), tungsten (W), iron (Fe), cobalt (Co), nickel (Ni), ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir) and platinum (Pt). Metals from the lanthanide and actinide series may also be used. Preferred are Fe, Ni, Co and mixtures thereof. Most preferred is a 50/50 mixture (by weight) of Ni and Co.

Detail Description Paragraph - DETX (108):

[0163] In the preferred process, the catalyst is formed, in situ, on the open tube ends of the molecular array by a vacuum deposition process. Any suitable equipment, such as that used in Molecular Beam Epitaxy (MBE) deposition, can be employed. One such device is a Kudsens Effusion Source Evaporator. It is also possible to effect sufficient deposition of metal by simply heating a wire in the vicinity of the tube ends (e.g., a Ni/CO wire or separate Ni and CO wires) to a temperature below the melting point at which enough atoms evaporate from one wire surface (e.g., from about 900 to about

1300.degree. C.). The deposition is preferably carried out in a vacuum with prior outgassing. Vacuums of about  $10^{-6}$  to  $10^{-8}$  Torr are suitable. The evaporation temperature should be high enough to evaporate the metal catalyst. Typically, temperatures in the range of 1500 to 2000.degree. C. are suitable for the Ni/Co catalyst of the preferred embodiment. In the evaporation process, the metal is typically deposited as monolayers of metal atoms. From about 1-10 monolayers will generally give the required amount of catalyst. The deposition of transition metal clusters on the open tube tops can also be accomplished by laser vaporization of metal targets in a catalyst deposition zone.

Detail Description Paragraph - DETX (113):

[0168] In the next step of the process of the present invention, the SWNT molecular array with catalyst deposited on the open tube ends is subjected to tube growth (extension) conditions. This may be in the same apparatus in which the catalyst is deposited or a different apparatus. The apparatus for carrying out this process will require, at a minimum, a source of carbon-containing feedstock and a means for maintaining the growing end of the continuous fiber at a growth and annealing temperature where carbon from the vapor can be added to the growing ends of the individual nanotubes under the direction of the transition metal catalyst. Typically, the apparatus will also have means for continuously collecting the carbon fiber. The process will be described for illustration purposes with reference to the apparatus shown in FIGS. 6 and 7.

Detail Description Paragraph - DETX (114):

[0169] The carbon supply necessary to grow the SWNT molecular array into a continuous fiber is supplied to the reactor 10, in gaseous form through inlet 11. The gas stream should be directed towards the front surface of the growing array 12. The gaseous carbon-containing feedstock can be any hydrocarbon or mixture of hydrocarbons including alkyls, acyls, aryls, aralkyls and the like, as defined above. Preferred are hydrocarbons having from about 1 to 7 carbon atoms. Particularly preferred are methane, ethane, ethylene, acetylene, acetone, propane, propylene and the like. Most preferred is ethylene. Carbon monoxide may also be used and in some reactions is preferred. Use of CO feedstock with preformed Mo-based nano-catalysts is believed to follow a different reaction mechanism than that proposed for in situ-formed catalyst clusters. See Dai.

Detail Description Paragraph - DETX (115):

[0170] The feedstock concentration is preferably as chosen to maximize the

rate of reaction, with higher concentrations of hydrocarbon giving faster growth rates. In general, the partial pressure of the feedstock material (e.g., ethylene) can be in the 0.001 to 1000.0 Torr range, with values in the range of about 1.0 to 10 Torr being preferred. The growth rate is also a function of the temperature of the growing array tip as described below, and as a result growth temperatures and feed stock concentration can be balanced to provide the desired growth rates.

Detail Description Paragraph - DETX (117):

[0172] The SWNT molecular array tip should be heated to a temperature sufficient to cause growth and efficient annealing of defects in the growing fiber, thus forming a growth and annealing zone at the tip. In general, the upper limit of this temperature is governed by the need to avoid pyrolysis of the feedstock and fouling of the reactor or evaporation of the deposited metal catalyst. For most feedstocks, this is below about 1300.degree. C. The lower end of the acceptable temperature range is typically about 500.degree. C., depending on the feedstock and catalyst efficiency. Preferred are temperatures in the range of about 500.degree. C. to about 1200.degree. C. More preferred are temperatures in the range of from about 700.degree. C. to about 1200.degree. C. Temperatures in the range of about 900.degree. C. to about 1100.degree. C. are the most preferred, since at these temperatures the best annealing of defects occurs. The temperature at the growing end of the cable is preferably monitored by, and controlled in response to, an optical pyrometer 14, which measures the incandescence produced. While not preferred due to potential fouling problems, it is possible under some circumstances to employ an inert sweep gas such as argon or helium.

Detail Description Paragraph - DETX (121):

[0176] The molecular array (template) may be removed from the fiber before or after growth by macroscopic physical separation means, for example by cutting the fiber with scissors to the desired length. Any section from the fiber may be used as the template to initiate production of similar fibers.

Detail Description Paragraph - DETX (122):

[0177] The continuous carbon fiber of the present invention can also be grown from more than one separately prepared molecular array or template. The multiple arrays can be the same or different with respect to the SWNT type or geometric arrangement in the array. Large cable-like structures with enhanced tensile properties can be grown from a number of smaller separate arrays as shown in FIG. 8. In addition to the masking and mating techniques described

above, it is possible to prepare a composite structure, for example, by surrounding a central core array of metallic SWNTs with a series of smaller circular non-metallic SWNT arrays arranged in a ring around the core array as shown in FIG. 9.

Detail Description Paragraph - DETX (123):

[0178] Not all the structures contemplated by this invention need be round or even symmetrical in two-dimensional cross section. It is even possible to align multiple molecular array seed templates in a manner as to induce nonparallel growth of SWNTs in some portions of the composite fiber, thus producing a twisted, helical rope, for example. It is also possible to catalytically grow macroscopic carbon fiber in the presence of an electric field to aid in alignment of the SWNTs in the fibers, as described above in connection with the formation of template arrays.

Detail Description Paragraph - DETX (129):

[0184] The supported or unsupported SWNT seed materials can be combined with a stable growth catalyst as described above, by opening SWNT molecule ends and depositing a metal atom cluster. Alternatively, the growth catalyst can be provided to the open end or ends of the seed molecules by evaporating a suspension of the seeds in a suitable liquid containing a soluble or suspended catalyst precursor. For example, when the liquid is water, soluble metal salts such as Fe (NO.sub.3).sub.3, Ni (NO.sub.3).sub.2 or CO (NO.sub.3).sub.2 and the like may be employed as catalyst precursors. In order to insure that the catalyst material is properly positioned on the open end(s) of the SWNT seed molecules, it may be necessary in some circumstances to derivitize the SWNT ends with a moiety that binds the catalyst nanoparticle or more preferably a ligand-stabilized catalyst nanoparticle.

Detail Description Paragraph - DETX (130):

[0185] In the first step of the random growth process the suspension of seed particles containing attached catalysts or associated with dissolved catalyst precursors is injected into an evaporation zone where the mixture contacts a sweep gas flow and is heated to a temperature in the range of 250-500.degree. C. to flash evaporate the liquid and provide an entrained reactive nanoparticle (i.e., seed/catalyst). Optionally this entrained particle stream is subjected to a reduction step to further activate the catalyst (e.g., heating from 300-500.degree. C. in H.sub.2). A carbonaceous feedstock gas, of the type employed in the continuous growth method described above, is then introduced into the sweep gas/active nanoparticle stream and the mixture is carried by the

sweep gas into and through a growth zone.

Detail Description Paragraph - DETX (135):

[0190] The macroscopic carbon fiber produced as described herein is made up of an aggregate of large number of single-wall nanotubes preferably in generally **parallel** orientation. While individual nanotubes may deviate from **parallel** orientation relative to any other individual nanotube, particularly for very short distances, over macroscopic distances the average orientation of all of the nanotubes preferably will be generally **parallel** to that of all other nanotubes in the assembly (macroscopic distances as described herein are generally considered to be greater than 1 micron). In one preferred form, the SWNTs will be arranged in a regular triangular lattice, i.e., in a closest packing relationship.

Detail Description Paragraph - DETX (136):

[0191] The carbon fiber of this invention is made up of individual tubular molecules and may be in whole or in part either crystalline or amorphous in structures. The degree of order in the fiber will depend both on the geometric relationship of the tubes in the molecular **array** and the growth and annealing conditions. The fiber may be subjected to orientation or other post-formation treatments before or after collection. The fiber produced by this process may, for example, be further spun or braided into larger yarns or cables. It is also contemplated that as produced fiber will be large enough in diameter for many applications.

Detail Description Paragraph - DETX (137):

[0192] Generally, the macroscopic carbon fiber produced according to this invention consists of a sufficient number of substantially **parallel** single-wall nanotubes that it is large enough in diameter to be practically handled as an individual fiber and/or process into larger continuous products. The macroscopic nature of the assembly of nanotubes is also important for end uses such as transmission of electric current over these nanotube cables. A macroscopic carbon fiber according to this invention preferably will contain at least  $10^{16}$  single-wall carbon nanotubes, and more preferably at least  $10^{19}$  single-wall carbon nanotubes. The number of assembled nanotubes is vastly larger than the number ( $<10^{13}$ ) that spontaneously **align** during the formation of single-wall nanotube ropes in the condensing carbon vapor of a carbon arc or laser vaporization apparatus. For many applications the preferred diameter of the macroscopic carbon fiber of this invention will be in the range of from about 1 to about 10 microns. Some applications, e.g., power

transmission cables, may require fiber diameters of up to a few centimeters. It is also possible to include dopants, e.g., metals, halogens,  $\text{FeCl}_3$  and the like, physically entrapped between the tubes of the fiber.

Detail Description Paragraph - DETX (140):

[0195] In a particular embodiment, macroscopic carbon fiber according to this invention is grown from a molecular **array** comprising a SAM having a region substantially comprising single-wall nanotubes in armchair orientation, the region having a diameter of at least one micron and preferably at least 100 microns. By use of masks on the surface upon which the monolayer is assembled, the area containing single-walled nanotubes in armchair structure is completely surrounded on all sides by a concentric region of tubes having a chiral or zig-zag structure. Elongation from this template will produce a conducting core surrounded by a semi-conducting or insulating sheath, each layer made up of single molecules of essentially infinite length. In a similar manner, a co-axial transmission cable with several layers can be produced.

Detail Description Paragraph - DETX (142):

[0197] The carbon fiber technology of this invention also facilitates a class of novel composites employing the hexaboronitride lattice. This material forms graphene-like sheets with the hexagons made of B and N atoms (e.g.,  $\text{B}_3\text{N}_2$  or  $\text{C}_2\text{BN}_3$ ). It is possible to provide an outer coating to a growing carbon fiber by supplying a BN precursor (e.g., tri-chloroborazine, a mixture of  $\text{NH}_3$  and  $\text{BCl}_3$  or diborane) to the fiber which serves as a mandrel for the deposition of BN sheets. This outer BN layer can provide enhanced insulating properties to the metallic carbon fiber of the present invention. Outer layers of pyrolytic carbon polymers or polymer blends may also be employed to impart. By changing the feedstock in the above described process of this invention from a hydrocarbon to a BN precursor and back again it is possible to grow a fiber made up of individual tubes that alternate between regions of all carbon lattice and regions of BN lattice. In another embodiment of this invention, an all BN fiber can be grown by starting with a SWNT template **array** topped with a suitable catalyst and fed BN precursors. These graphene and BN systems can be mixed because of the very close match of size to the two hexagonal units of structure. In addition, they exhibit enhanced properties due to the close match of coefficients of thermal expansion and tensile properties. BN fibers can be used in composites as reinforcing and strengthening agents and many of the other uses described above for carbon fibers.

Detail Description Paragraph - DETX (144):

[0199] The unique properties of the tubular carbon molecules, molecular arrays and macroscopic carbon fibers of the present invention provide exciting new device fabrication opportunities.

Detail Description Paragraph - DETX (153):

[0208] A Grtzel cell of the type described in U.S. Pat. No. 5,084,365 (incorporated herein by reference in its entirety) can be fabricated with the nanocrystalline  $\text{TiO}_2$  replaced by a monolayer molecular array of short carbon nanotube molecules as described above. The photoactive dye need not be employed since the light energy striking the tubes will be converted into an oscillating electronic current which travels along the tube length. The ability to provide a large charge separation (the length of the tubes in the array) creates a highly efficient cell. It is also contemplated by the present invention to use a photoactive dye (such as cis-[bisthiacyanato bis (4,4'-dicarboxy-2,2'-bipyridine Ru (II))] attached to the end of each nanotube in the array to further enhance the efficiency of the cell. In another embodiment of the present invention, the  $\text{TiO}_2$  nanostructure described by Grtzel can serve as an underlying support for assembling an array of SWNT molecules. In this embodiment, SWNTs are attached directly to the  $\text{TiO}_2$  (by absorptive forces) or first derivatized to provide a linking moiety and then bound to the  $\text{TiO}_2$  surface. This structure can be used with or without a photoactive dye as described above.

Detail Description Paragraph - DETX (159):

[0214] A memory device can be constructed using either a two- or three-dimensional array of the elements shown in FIG. 12. Because the elements of the memory array are so small (i.e., about 5 nm.times.25 nm), extremely high bit densities can be achieved, i.e.,  $>1.0 \text{ terabit/cm}^2$  (i.e., a bit separation of 7.5 nm). Because the bucky ball only has to move a few nanometers and its mass is so small, the write time of the described device is on the order of 10<sup>-10</sup> seconds.

Detail Description Paragraph - DETX (161):

[0216] The present invention also relates to a lithium ion secondary battery in which the anode material includes a molecular array of SWNTs made as described above (e.g., by SAM techniques). The anode material can comprise a large number (e.g.,  $>10^3$ ) short nanotube molecules bound to a substrate. Alternatively, the end of a macroscopic carbon fiber as described above can serve as the microporous anode sure.

Detail Description Paragraph - DETX (162):

[0217] The tubular carbon molecules in this array may be open or closed. In either case, each tubular carbon molecule provides a structurally stable microporosity for the intercalation of lithium ions, i.e., into the open tubes or into triangular pores of an end cap. The resulting fullerene intercalation compound (FIC) can be used, for example, with an aprotic organic electrolyte containing lithium ions and a  $\text{LiCoO}_2$  cathode to form an improved lithium ion secondary battery of the type described in Nishi, "The Development of Lithium Ion Secondary Batteries," 1996 IEEE symposium on VLSI Circuits and shown in FIG. 13. In this figure, the anode 50 comprises a large number of SWNTs 51 in an ordered molecular array. Cathode 52, electrolyte 53, lithium ions 54 and electrons 55 make up the remaining elements of the cell.

Detail Description Paragraph - DETX (163):

[0218] The use of the molecular array FICs of this invention provides a lithium-storing medium that has a high charge capacity (i.e.,  $>600 \text{ mA h/g}$ ) which is stable during charging and possesses excellent cyclability and that results in an improved safe rechargeable battery.

Detail Description Paragraph - DETX (177):

[0232] A design for such an anode is one which consists of an array of fullerene nanotubes, attached to a metallic support electrode, such as gold-coated copper, and arranged in a hexagonal lattice much like a bed of nails. As shown in FIG. 14, this structure has the virtue that the storage area for the reduced state of the lithium,  $\text{Li}^0$ , is down deep channels either between the nanotubes or down the hollow core of the tubes themselves. Accordingly, the redox chemistry of the lithium is confined primarily to the exposed ends of the nanotubes, and here derivatization of the nanotube ends provides great opportunities to insure that this redox chemistry is as reversible as possible.

Detail Description Paragraph - DETX (184):

[0239] The geometric structure may also have electromagnetic properties that include converting electromagnetic energy to electrical current, an antenna, an array of antennae, an array that produces coherent interference of electromagnetic waves to disperse those of different wavelength, an array that selectively modifies the propagation of electromagnetic waves, or an element that interacts with optical fiber. The electromagnetic property can be

selectively determined by the FSA and the interaction of and among FSAs. For example, the lengths, location, and orientation of the molecules can be determined by FSAs so that an electromagnetic field in the vicinity of the molecules induces electrical currents with some known phase relationship within two or more molecules. The spatial, angular and frequency distribution of the electromagnetic field determines the response of the currents within the molecules. The currents induced within the molecules bear a phase relationship determined by the geometry of the array. In addition, application of the FSAs could be used to facilitate interaction between individual tubes or groups of tubes and other entities, which interaction provides any form of communication of stress, strain, electrical signals, electrical currents, or electromagnetic interaction. This interaction provides an "interface" between the self-assembled nanostructure and other known useful devices.

Detail Description Paragraph - DETX (193):

[0248] Further, these individual nanotube antenna elements can be combined to form an antenna array. The lengths, location, and orientation of the molecules are chosen so that electrical currents within two or more of the molecules act coherently with some known phase relationship, producing or altering an electromagnetic field in the vicinity of the molecules. This coherent interaction of the currents within the molecules acts to define, alter, control, or select the spatial, angular and frequency distributions of the electromagnetic field intensity produced by the action of these currents flowing in the molecules. In another embodiment, the currents induced within the molecules bear a phase relationship determined by the geometry of the array, and these currents themselves produce a secondary electromagnetic field, which is radiated from the array, having a spatial, angular and frequency distribution that is determined by the geometry of the array and its elements. One method of forming antenna arrays is the self-assembly monolayer techniques discussed above.

Detail Description Paragraph - DETX (199):

[0254] The SWNT molecules of the present invention also enable the fabrication of probes and manipulators on a nanoscale. Probe tips for AFM and STM equipment and AFM cantilevers are examples of such devices. Derivatized probes can serve as sensors or sensor arrays that effect selective binding to substrates. Devices such as these can be employed for rapid molecular-level screening assays for pharmaceuticals and other bioactive materials. Further, conducting SWNT molecules of the present invention may also be employed as an electrochemical probe.

Detail Description Paragraph - DETX (203):

[0258] Although composites are generally extremely strong, their strength is generally anisotropic, being much less in the direction **perpendicular** to the plane of the composite material than any **parallel** direction. Because of this characteristic, composites that are formed in layers or in laminate strips are prone to delamination. Delamination may occur when at least one layer of the composite separates from the others, resulting in a void in the bulk of the composite material. This void is exceedingly difficult to detect, and with repeated applications of stress to the composite element, the composite element will fail catastrophically, without warning.

Detail Description Paragraph - DETX (212):

[0267] The nanotubes, ropes, or fibers used in the composites may also be derivatized as described above. End cap derivatization of carbon nanotubes can facilitate the bonding of the carbon nanotubes to each other or to the matrix material. While pure carbon nanotubes generally contain side walls that are entirely uniform (consisting of an **array** of the hexagonal carbon lattice similar to that of graphite), it is possible to introduce defects or create bonding sites in the sidewalls to facilitate bonding adhesion to the matrix material. One example would be to incorporate an impurity such as Boron atoms in the side wall. The wall defect or bonding site thus created may facilitate interaction of the nanotube with the matrix material through physical or chemical forces. It is additionally possible that such defect or bonding site may facilitate chemical reactions between the tube itself and the matrix material in a way that affects the properties of the composite material formed. As described above, the carbon nanotube material may also have a part of its lattice replaced with boron nitride.

Detail Description Paragraph - DETX (220):

[0275] The unique properties of the carbon fiber produced by the present invention also permit new types of composite reinforcement. It is possible, for example, to produce a composite fiber/polymer with anisotropic properties. This can, for example, be accomplished by dispersing a number of metallic carbon nanotube fibers (e.g., from (n,n) SWNTs) in a prepolymer solution (e.g., a poly methymethacrylate) and using an external electric field to **align** the fibers, followed by polymerization. Electrically conductive components can also be formed using the metallic forms of carbon nanotubes.

Detail Description Paragraph - DETX (229):

[0281] The flowing metal concentrations were used in this example: cobalt (1.0 atom percent), copper (0.6 atom percent), niobium (0.6 atom percent), nickel (0.6 atom percent), platinum (0.2 atom percent), a mixture of cobalt and nickel (0.6 atom percent/0.6 atom percent respectively), a mixture of cobalt and platinum (0.6 atom percent/0.2 atom percent respectively), a mixture of cobalt and copper (0.6 atom percent/0.5 atom percent respectively), and a mixture of nickel and platinum (0.6 atom percent/0.2 atom percent respectively). The remainder of the mixture was primarily graphite along with small amounts of carbon cement. Each target was vaporized with a laser beam and the soots collected from the water cooled collector were then collected separately and processed by sonicating the soot for 1 hour in a solution of methanol at room temperature and pressure (other useful solvents include acetone, 1,2-dichloroethane, 1-bromo, 1,2-dichloroethane, and N,N-dimethylformamide). With one exception, the products collected produced a homogeneous suspension after 30 to 60 minutes of sonication in methanol. One sample vaporized from a mixture of cobalt, nickel and graphite was a rubbery deposit having a small portion that did not fully disperse even after 2 hours of sonication in methanol. The soots were then examined using a transmission electron microscope with a beam energy of 100 keV (Model JEOL 2010).

#### Detail Description Paragraph - DETX (232):

[0284] The images shown in FIGS. 15A through 15E are transmission electron micrographs of single-wall carbon nanotubes produced by vaporizing a target comprising graphite and a mixture of cobalt and nickel (0.6 atom percent/0.6 atom percent respectively) at an oven temperature of 1200.degree. C. FIG. 15A shows a medium-magnification view (where the scale bar represents 100 nm) showing that almost everywhere, bundles of single-wall carbon nanotubes are tangled together with other single-wall carbon nanotubes. FIG. 15B is a high-magnification image of one bundle of multiple single-wall carbon nanotubes that are all roughly parallel to each other. The single-wall carbon nanotubes all have a diameter of about 1 nm, with similar spacing between adjacent single-wall carbon nanotubes. The single-wall carbon nanotubes adhere to one another by van der Waals forces.

#### Detail Description Paragraph - DETX (233):

[0285] FIG. 15C shows several overlapping bundles of single-wall carbon nanotubes, again showing the generally parallel nature of each single-wall nanotube with other single-wall carbon nanotubes in the same bundle, and showing the overlapping and bending nature of the various bundles of single-wall carbon nanotubes. FIG. 15D shows several different bundles of single-wall carbon nanotubes, all of which are bent at various angles or arcs.

One of the bends in the bundles is relatively sharp, illustrating the strength and flexibility of the bundle of single-wall carbon nanotubes. FIG. 15E shows a cross-sectional view of a bundle of 7 single-wall carbon nanotubes, each running roughly parallel to the others. All of the transmission electron micrographs in FIGS. 15A through 15E clearly illustrate the lack of amorphous carbon overcoating that is typically seen in carbon nanotubes and single-wall carbon nanotubes grown in arc-discharge methods. The images in FIG. 15A through 15E also reveal that the vast majority of the deposit comprises single-wall carbon nanotubes. The yield of single-wall carbon nanotubes is estimated to be about 50% of the carbon vaporized. The remaining 50% consists primarily of fullerenes, multi-layer fullerenes (fullerene onions) and/or amorphous carbon.

Detail Description Paragraph - DETX (234):

[0286] FIGS. 15A through 15E show transmission electron microscope images of the products of the cobalt/nickel catalyzed carbon nanotube material that was deposited on the water cooled collector in the laser vaporization apparatus depicted in FIG. 1. Single-wall carbon nanotubes were typically found grouped in bundles in which many tubes ran together roughly parallel in van der Waals contact over most of their length. The grouping resembled an "highway" structure in which the bundles of single-wall carbon nanotubes randomly criss-crossed each other. The images shown in FIG. 15A through 15E make it likely that a very high density of single-wall carbon nanotubes existed in the gas phase in order to produce so many tubes aligned as shown when landing on the cold water cooled collector. There also appeared to be very little other carbon available to coat the single-wall carbon nanotubes prior to their landing on the water cooled collector in the alignment shown. Evidence that single-wall carbon nanotubes grow in the gas phase, as opposed to for example on the walls of the quartz tube was provided in earlier work on multi-walled carbon nanotubes using the same method. See Guo et al., "Self-Assembly of Tubular Fullerenes," J. Phys. Chem., Vol. 99, p. 10694 (1995) and Saito et al., "Extrusion of Single-Wall Carbon Nanotubes via Formation of Small Particles Condensed Near An Evaporation Source," Chem. Phys. Lett., Vol. 236, p. 419 (1995). The high yield of single-wall carbon nanotubes in these experiments is especially remarkable because the soluble fullerene yield was found to be about 10 weight percent, and much of the remaining carbon in the soot product consisted of giant fullerenes and multi-layer fullerenes.

Detail Description Paragraph - DETX (243):

[0291] About 2 mg of the raw product mat was sonicated in 5 ml methanol for about 0.5 hour at room temperature. Transmission Electron Microscope (TEM)

analysis of the sonicated product proved that the product was comprised mostly of ropes of single-wall carbon nanotubes, i.e., bundles of 10 to 1000 single-wall carbon nanotubes aligned with each other (except for occasional branching) having a reasonably constant rope diameter over the entire length of the rope. The ropes were more than 100 microns long and consisting of uniform diameter single-wall carbon nanotubes. About 70to90 wt % of the product is in the form of ropes. The individual single-wall carbon nanotubes in the ropes all terminate within 100 nm of each other at the end of the rope. More than 99% of the single-wall carbon nanotubes appear to be continuous and free from carbon lattice defects over all of the length of each rope.

Detail Description Paragraph - DETX (252):

Assembly of a SWNT array

Detail Description Paragraph - DETX (253):

[0295] About 10.sup.6 (10,10) nanotube molecules with lengths 50-60 nm are prepared as described above, are derivatized to have an -SH group at one end and allowed to form a SAM molecular array of SWNT molecules on a substrate coated with gold in which the tubular molecules are aligned with their long axis parallel and the ends of the tubes forming a plane perpendicular to the aligned axes.

Detail Description Paragraph - DETX (256):

[0296] The array according to Example 6 can be used to grow a continuous macroscopic carbon fiber in the apparatus shown in FIGS. 6 and 7. The ends of the nanotubes (which form the plane perpendicular to the axes of the tubes) of the array are first opened. For the 2D assembly of nanotubes on the gold covered surface, the assembly can be made to be the positive electrode for electrolytic etching in 0.1 M KOH solution, which will open the tips of the nanotubes.

Detail Description Paragraph - DETX (257):

[0297] Ni/Co metal clusters are then vacuum deposited onto the open ends of the assembled nanotubes in the SAM. Preferably, metal clusters 1 nm in diameter are arranged so that one such Ni/Co nanoparticle sits on the top opening of every nanotube in the nanotube array.

Detail Description Paragraph - DETX (258):

[0298] The Ni/Co capped nanotubes in the array are heated in a vacuum up to 600.degree. C. pyrolyzing off all but the carbon nanotubes and the Ni/Co particles. Once the pyrolysis is complete, a flow of ethylene gas is started, and the tubes elongate in the direction of the aligned axes to form a carbon fiber of macroscopic diameter. If a significant portion of the Ni/Co catalyst particles deactivate, it may be necessary to electrochemically etch the tips open and clean the assembly again, and repeat steps of applying the Ni/Co catalyst particles and reinitiating growth of the array. A continuous fiber of about 1 micro in diameter is continuously recovered at room temperature on the take-up roll.

Detail Description Paragraph - DETX (266):

[0304] The cut fullerene tubes material formed stable colloidal suspensions in water with the assistance of surfactants such as sodium dodecyl sulfate or a non-ionic surfactant such as Triton X-100. The suspensions were separated as a function of nanotube length.

Detail Description Paragraph - DETX (270):

[0306] Referring to FIGS. 16A-C, a SEM image of raw SWNT felt material is shown in FIG. 16A, while the same material after purification is shown in FIGS. 16B-C. The abnormally low quality initial starting material emphasizes the effectiveness of the following purification process. The raw sample (8.5 gm) was refluxed in 1.21 of 2.6 M nitric acid for 45 hours. Upon cooling, the solution was transferred to PTFE centrifuge tubes and spun at 2400 g for 2 hours. The supernatant acid was decanted off, replaced by de-ionized water, vigorously shaken to resuspend the solids, followed by a second centrifuge/decant cycle. The solids were re-suspended in 1.8 l water with 20 l Triton X-100 surfactant and adjusted to a pH of 10 with sodium hydroxide. The suspension was then transferred to the reservoir of a tangential flow filtration system (MiniKros Lab System, Spectrum, Laguna Hills, Calif.). The filter cartridge used (M22M 600 0.1N, Spectrum) had mixed cellulose ester hollow fibers of 0.6 mm diameter, 200 nm pores and a total surface area of 5600 cm.sup.2. The buffer solution consisted of 44 l of 0.2 vol % Triton X-100 in water of which the first 34 l were made basic (pH 10) with sodium hydroxide, and the final 10 l at pH 7. The cartridge inlet pressure was maintained at 6 psi. A control valve was added to the exit so that the outflow rate was restricted to 70 ml min.sup.-1. The result was a stable suspension of purified SWNT for which the SEM image in FIG. 16B is typical. Filtration of this suspension produces a paper of tangled SWNT which resembles carbon paper in appearance and feel. As is evident in the SEM image of FIG. 16C, the torn edge of this "bucky paper" shows that the tearing process produces a substantial

alignment of SWNT rope fibers. The overall yield of purified SWNT from this abnormally poor starting material was 9% by weight.

Detail Description Paragraph - DETX (271):

[0307] FIG. 17 shows a tapping mode AFM image of cut fullerene nanotubes (pipes) electrodeposited from a stable colloidal suspension onto highly oriented pyrolytic graphite (HOPG). The tubes had a tendency to align 120.degree. to one another. They are in registry with the underlying graphite lattice. AFM measurements of the heights of these cut tubes revealed that roughly half were single tubes 1-2 nm in diameter, whereas the rest are aggregates of several tubes in van der Waals contact. These cut tubes were prepared in a two step process: cutting and polishing. In a typical example, 10 mg of the purified SWNT "bucky paper" (shown in FIG. 16B) was suspended in 40 ml of a 3:1 mixture of concentrated H.sub.2SO.sub.4/HNO.sub.3 in a 100 ml test tube and sonicated in a water bath (Cole Palmer model B3-R, 55 kHz) for 24 hours at 35-40 .degree. C. The resultant suspension was then diluted with 200 ml water and the larger cut SWNT tubes were caught on a 100 nm pore size filter membrane (type VCTP, Millipore Corp., Bedford, Mass.) and washed with 10 mM NaOH solution. These cut tubes were then further polished (chemically cleaned) by suspension in a 4:1 mixture of concentrated H.sub.2SO.sub.4: 30% aqueous H.sub.2O.sub.2 and stirring at 70.degree. C. for 30 minutes. After filtering and washing again on a 100 nm filter, the cut nanotubes were suspended at a density of 0.1 mg/ml in water with the aid of 0.5 wt % Triton X-100 surfactant. The electrodeposition was performed by placing 20 .mu.l of the nanotube suspension on the of a freshly cleaved HOPG substrate (Advanced Ceramics, Cleveland, Ohio), confining the droplet within a Vitron O-ring (4 mm o.d., 1.7 mm thick), capping the trapped suspension with a stainless steel electrode on top of the O-ring, and applying a steady voltage of 1.1V for 6 minutes. When suspended in water, the nanotubes are negatively charged and are therefore driven by the electric field onto the HOPG surface. After deposition the HOPG/nanotube surface was washed with methanol on a spin-coater in order to remove the water and the Triton X-100 surfactant.

Detail Description Paragraph - DETX (272):

[0308] FIG. 18 shows the Field Flow Fractionation (FFF) of cut fullerene nanotube "pipes" in aqueous suspension. A 20 .mu.l sample of 0.07 mg/mg cut nanotube suspension in 0.5% aqueous Triton X-100 was injected into a cross-flow FFF instrument (Model F-1000-OF, FFFractionation, LLC, Salt Lake City, Utah) operating with 0.007% Triton X-100 in water mobile phase at 2 ml min.sup.31 1, and a cross-flow rate of 0.5 ml min.sup.-1. The solid curve (left vertical axis) of FIG. 18A shows the light scattering turbidity (at 632.8 nm wavelength).

of the eluting nanotubes as a function of total eluent volume since ejection. The open circles (right axis) plot the estimate radius of gyration of the nanotubes as measured by a 16 angle light scattering instrument (DAWN DSP, Wyatt Technology, Santa Barbara, Calif.). FIGS. 18B, 18C, and 18D show nanotube length distributions from FFF eluent fractions 1, 3, and 5, respectively, as measured from AFM images of the suspended fullerene nanotubes electrodeposited on HOPG as in FIG. 17.

Detail Description Paragraph - DETX (273):

[0309] FIG. 19 shows an AFM image of a fullerene nanotube "pipe" tethered to two 10 nm gold spheres, one at either end. The tube was electrodeposited onto HOPG graphite from a suspension of a mixture of such tubes with colloidal gold particles (Sigma Chemical Co.) in water. The irregularly shaped features in the image are due to residual deposits of the Triton X-100 surfactant used to stabilize the suspension. The nanotube-to-gold tethers were constructed of alkyl thiol chains covalently attached to the open ends of the tubes. Presuming these open ends were terminated with many carboxylic acid groups as a result of the acid etching in previous processing, they were converted to the corresponding acid chloride by reacting them with  $\text{SOCl}_2$ . These derivitized tubes were then exposed to  $\text{NH}_2-(\text{CH}_2)_{16}-\text{SH}$  in toluene to form the desired tethers, with the thiol group providing a strong covalent bonding site for a gold particle. Most tubes derivitized this way have a single gold particle bound to at least one of their ends, as revealed by extensive AFM imaging.

Detail Description Paragraph - DETX (277):

[0311] Alternatively, a carbon fiber, fullerene nanotube composite can be prepared by drawing one or more continuous carbon fibers or woven carbon fiber tapes through a vat containing the above dichloroethane epoxy nanotube suspension, and then winding this impregnated tape around a desired form. After curing in an autoclave in a fashion known in the carbon fiber-epoxy composite industry (see, e.g., D. L. Chung, Carbon Fiber Composites (1994)), a composite of superior delamination resistance is produced. The fullerene nanotubes within the composite strengthen the epoxy between the carbon-fiber layers. A superior composite is produced if one uses fullerene fibers for both the woven tape layers and the tangled nanotube strengtheners within the epoxy phase.

Claims Text - CLTX (25):

24. The method of claim 18 wherein said cutting single-wall nanotubes into

tubular carbon molecules comprises the steps of: (a) forming a suspension of single-wall nanotubes in a medium; (b) sonicating said suspension with acoustic energy.

Claims Text - CLTX (32):

31. A method for forming a macroscopic molecular array of tubular carbon molecules, said method comprising the steps of: (a) providing at least about 10.sup.6 tubular carbon molecules of substantially similar length in the range of 50 to 500 nm; (b) introducing a linking moiety onto at least one end of said tubular carbon molecules; (c) providing a substrate coated with a material to which said linking moiety will attach; and (d) contacting said tubular carbon molecules containing a linking moiety with said substrate.

Claims Text - CLTX (35):

34. A method for forming a macroscopic molecular array of tubular carbon molecules, said method comprising the steps of: (a) providing a nanoscale array of microwells on a substrate; (b) depositing a metal catalyst in each of said microwells; and (c) directing a stream of hydrocarbon or CO feedstock gas at said substrate under conditions that effect growth of single-wall carbon nanotubes from each microwell.

Claims Text - CLTX (37):

36. A method for forming a macroscopic molecular array of tubular carbon molecules, said method comprising the steps of: (a) providing surface containing purified but entangled and relatively endless single-wall carbon nanotube material; (b) subjecting said surface to oxidizing conditions sufficient to cause short lengths of broken nanotubes to protrude up from said surface; and (c) applying an electric field to said surface to cause said nanotubes protruding from said surface to align in an orientation generally perpendicular to said surface and coalesce into an array by van der Waals interaction forces.

Claims Text - CLTX (39):

38. A method of forming a macroscopic molecular array of tubular carbon molecules, said method comprising the step of assembling subarrays of up to 16 single-wall carbon nanotubes into a composite array.

Claims Text - CLTX (43):

42. A method for continuously growing macroscopic carbon fiber comprising at least about 10.sup.6 single-wall nanotubes in generally **parallel** orientation, said method comprising the steps of: (a) providing a macroscopic molecular **array** of at least about 10.sup.6 tubular carbon molecules in generally **parallel** orientation and having substantially similar lengths in the range of from about 50 to about 500 nanometers; (b) removing the hemispheric fullerene cap from the upper ends of the tubular carbon molecules in said **array**; contacting said upper ends of the tubular carbon molecules in said **array** with at least one catalytic metal; (d) supplying a gaseous source of carbon to the end of said **array** while applying localized energy to the end of said **array** to heat said end to a temperature in the range of about 500.degree. C. to about 1300.degree. C.; and (e) continuously recovering the growing carbon fiber.

Claims Text - CLTX (82):

81. A macroscopic molecular **array** comprising at least about 10.sup.6 single-wall carbon nanotubes in generally **parallel** orientation and having substantially similar lengths in the range of from about 5 to about 500 nanometers.

Claims Text - CLTX (83):

82. The **array** of claim 81 wherein said nanotubes are of the same type.

Claims Text - CLTX (84):

83. The **array** of claim 82 wherein said nanotubes are of the (n,n) type.

Claims Text - CLTX (85):

84. The **array** of claim 83 wherein said nanotubes are of the (10,10) type.

Claims Text - CLTX (86):

85. The **array** of claim 83 wherein said nanotubes are of the (m,n) type.

Claims Text - CLTX (87):

86. The **array** of claim 81 wherein said nanotubes are of different types.

Claims Text - CLTX (88):

87. The array of claim 81 further comprising a substrate attached to one end of said array and oriented substantially perpendicularly to the nanotubes in said array.

Claims Text - CLTX (89):

88. The array of claim 87 wherein said substrate is a bucky paper surface.

Claims Text - CLTX (90):

89. The array of claim 87 wherein said substrate is a metal layer selected from the group consisting of gold, mercury and indium-tin-oxide.

Claims Text - CLTX (91):

90. The array of claim 86 wherein a central portion of nanotubes are of the (n,n) type and an outer portion of nanotubes are of the (m,n) type.

Claims Text - CLTX (92):

91. A macroscopic carbon fiber comprising at least about 10<sup>sup.6</sup> single-wall carbon nanotubes in generally parallel orientation.

Claims Text - CLTX (95):

94. A molecular template array for growing continuous length carbon fiber comprising a segment of the fiber of claim 91.

Claims Text - CLTX (105):

104. A solar cell for converting broad spectrum light energy into electrical current comprising a molecular array according to claim 81 as the photon collector.

Claims Text - CLTX (106):

105. The solar cell of claim 104 additionally comprising a photoactive dye coupled to the upper ends of the nanotubes in said array.

Claims Text - CLTX (112):

111. A microporous anode for an electrochemical cell comprising a molecular array according to claim 81.

Claims Text - CLTX (114):

113. An apparatus for forming a continuous macroscopic carbon fiber from a macroscopic molecular template **array** comprising at least about 10.sup.6 single-wall carbon nanotubes having a catalytic metal deposited on the open ends of said nanotubes, said apparatus comprising: (a) means for locally heating only said open ends of said nanotubes in said template **array** in a growth and annealing zone to a temperature in the range of about 500.degree. C. to about 1300.degree. C.; (b) means for supplying a carbon-containing feedstock gas to the growth and annealing zone immediately adjacent said heated open ends of said nanotubes in said template **array**; and (c) means for continuously removing growing carbon fiber from said growth and annealing zone while maintaining the growing open end of said fiber in said growth and annealing zone.

Claims Text - CLTX (138):

137. The method of claim 136, wherein said fibrous materials are arranged in a two-dimensional sheet, and some portion of the said carbon nanotube material is oriented in a direction other than **parallel** to said sheet.

Claims Text - CLTX (156):

155. An **array** of light harvesting antennas of claim 153.

Claims Text - CLTX (157):

156. The **array** of light harvesting antennas of claim 155, wherein said **array** is formed by self-assembly.